DEVELOPMENT OF MACROSCOPIC NANOPOROUS GRAPHENE MEMBRANES FOR GAS SEPARATION

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Development of macroscopic nanoporous graphene membranes for gas separation

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Abstract

Separating components of a gas from a mixture is a critical step in several important industrial processes including natural gas purification, hydrogen production, carbon dioxide sequestration, and oxy-combustion. For such applications, gas separation membranes are attractive because they offer relatively low energy costs but can be limited by low flow rates and low selectivities.

Nanoporous graphene membranes have the potential to exceed the permeance and selectivity limits of existing gas separation membranes. This is made possible by the atomic thickness of the material, which can support sub-nanometer pores that enable molecular sieving while presenting low resistance to permeate flow. The feasibility of gas separation by graphene nanopores has been demonstrated experimentally on micron-scale areas of graphene. However, scaling up to macroscopic sizes presents significant challenges, including graphene imperfections and control of the selective nanopore size distribution across large areas. The overall objective of this thesis research is to develop macroscopic graphene membranes for gas separation.

Investigation reveals that the inherent permeance of large areas of graphene results from the presence of micron-scale tears and nanometer-scale intrinsic defects. Stacking multiple graphene layers is shown to reduce leakage exponentially.

A model is developed for the inherent permeance of multi-layer graphene and shown to accurately explain measured flow rates. Applying this model to membranes with created selective pores, it is predicted that by proper choice of the support membrane beneath graphene or adequate leakage sealing, it should be possible to construct a selectively permeable graphene membrane despite the presence of defects.

Interfacial polymerization and atomic layer deposition steps during membrane fabrication are shown to effectively seal micron-scale tears and nanometer-scale defects in graphene. The support membrane is designed to isolate intrinsic defects and reduce leakage through tears.

Methods of creating a high density of selectively permeable nanopores are explored. Knudsen selectivity is achieved using macroscopic three-layer graphene membranes on polymer supports by high density ion bombardment. Separation ratios exceeding the Knudsen effusion limit are achieved with single-layer graphene on optimized supports by low density ion bombardment followed by oxygen plasma etching, providing evidence of molecular sieving based gas separation through centimeter-scale graphene membranes.

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Chapter 1

Introduction

Separating the components of a gas mixture is an important step in several industrial processes.\textsuperscript{1,2} Natural gas is purified prior to distribution to enhance quality, improve safety, and increase revenue. This involves the removal of carbon dioxide (CO\textsubscript{2}), nitrogen (N\textsubscript{2}), hydrogen sulfide (H\textsubscript{2}S), water vapor (H\textsubscript{2}O), and heavier hydrocarbons from methane (CH\textsubscript{4}). The production of ammonia for fertilizer and some oil refinement processes require H\textsubscript{2}. This is commonly produced by stream reformation of CH\textsubscript{4}. H\textsubscript{2} is separated from carbon monoxide (CO) in the resulting syngas. H\textsubscript{2} recovery from light hydrocarbons, Ar, and N\textsubscript{2} are other gas separation processes that can improve efficiency in oil refinement and ammonia production. N\textsubscript{2} is often employed in applications where a dry inert gas is required, such as food storage, high temperature manufacturing, and fire safety systems. It is produced by separation from air. Oxygen (O\textsubscript{2}) / air separation is also important for oxy-combustion in high thrust propulsion, welding, and high temperature furnaces used for glass production. Carbon capture systems for reducing the environmental impact of industrial processes require CO\textsubscript{2} / N\textsubscript{2} separation. Organic vapor separation is essential in refineries and petrochemical plants.
Gas separation is accomplished by sorption, distillation, or membrane processes. Sorption based systems use a sorbent material that can accumulate a large volume of one gas species to remove it from a mixed gas stream. Activated carbon and zeolites are examples of solid sorbents that have very high surface area for gas adsorption. The primary means of removing CO₂ and H₂S from natural gas is absorption into liquid amines. These processes require regeneration of the sorbent, which is energy intensive.

Distillation systems separate mixtures based on differences in the boiling points of the constituent gases. Heating and cooling the mixture is also energy intensive; distillation columns for separating hydrocarbons use 40-60% of the total energy consumed by oil refineries.

Membranes separate gases using a material that is selectively permeable to certain components of the mixture. These systems have low energy costs compared to sorption and distillation methods. However, there is an inherent trade-off between the permeance and selectivity of conventional membranes operating by a solution-diffusion mechanism that has traditionally limited gas separation membranes to systems requiring relatively low production rates or to mixtures with high impurity concentrations in the feed gas. Box 1-1 summarizes important terms related to gas separation membranes.

Membranes have found use primarily in N₂/air, CO₂/natural gas, H₂/Ar, H₂/N₂, and H₂/CH₄ separations. Increasing the share of membrane technology in the gas separation market requires further improvements in permeance to meet the production needs of industrial processes. For example, existing membranes for CO₂/N₂ separation have selectivities of 30 to 60, sufficient for carbon capture, but the achievable permeances are prohibitively low for this application. Novel membrane materials have the greatest potential to produce the significant enhancements in permeance that are required to extend membrane usage into other applications.
Box 1-1. Membrane gas transport definitions, key equations, and length scales.

### Definitions of transport properties

**Permeance:** \( Q \equiv \frac{\dot{n}}{A_m} \Delta P \) [mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)]; GPU, where \( \dot{n} \) [mol s\(^{-1}\)] is the net mass/volume/molar flow rate across area \( A_m \) [m\(^2\)] of the membrane. Gas permeance is often reported in gas permeation units (GPU) instead of SI units, where 1 GPU = \( 3.35 \times 10^{-10} \) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) (Ref. 21).

**Selectivity:** \( S \equiv Q_A/Q_B \), where \( Q_A \) and \( Q_B \) are the membrane permeances of species A and B, respectively (flow rates of one species may be influenced by another).

**Pore permeation coefficient:** \( \Pi \equiv \frac{\dot{n}}{\Delta P} \) [mol s\(^{-1}\) Pa\(^{-1}\)], where \( \Delta P \) [Pa] is the pressure difference (or more generally, any driving force) across the pore.

**Pore effective area:** \( A_{eff} \equiv \Pi/J_{ideal\ gas} \) [m\(^2\)], where \( J_{ideal\ gas} \) [mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)] is the ideal gas flux.

### Relevant parameters

**Ideal gas mean free:** \( \lambda = k_B T / \sqrt{2} \pi d_g^2 P \) [m] where \( k_B \) [J/K] is Boltzmann’s constant, \( T \) [K] is the absolute temperature, \( d_g \) [m] is the gas molecule diameter, and \( P \) [Pa] is the pressure.

**Knudsen number:** \( Kn = \lambda / d \), where \( d \) [m] is the support pore diameter.

### Transport equations

**Ideal gas flux:** \( J_{ideal\ gas} = \frac{\Delta P}{2\pi M \bar{R} T} \) [mol m\(^{-2}\) s\(^{-1}\)], where \( M \) [kg mol\(^{-1}\)] is the molecular weight of the gas and \( \bar{R} \) [J mol\(^{-1}\) K\(^{-1}\)] is the universal gas constant. \( \dot{n} = J_{ideal\ gas} \pi d^2 / 4 \) [mol s\(^{-1}\)].

**Knudsen diffusion:** \( \dot{n} = \pi d^2 \Delta P / 3L \sqrt{2\pi M \bar{R} T} \) [mol s\(^{-1}\)], where \( L \) [m] is the pore length.

**Poiseuille flow:** \( \dot{n} = (\pi d^4 / 12\mu L) \Delta P (\bar{P} / \bar{R} T) \) [mol s\(^{-1}\)] where \( \mu \) [Pa s] is the dynamic viscosity and \( \bar{P} \) [Pa] is the average of the upstream and downstream pressure.

**Fickian diffusion:** \( \dot{n} = \kappa \pi d^2 \Delta P / 4L \bar{R} T \) [mol s\(^{-1}\)], where \( D \) [m\(^2\) s\(^{-1}\)] is the diffusion coefficient.

### Length Scales

**Graphene:** Carbon van der Waals diameter: \( 2R_{vdw} = 3.4 \) Å. Carbon bond length in graphene: \( a = 1.42 \) Å. Area of a hexagonal ring in graphene: \( A_0 = 5.24 \) Å\(^2\).

**Pore geometry:** \( D_c \) is pore diameter defined by centers of edge atoms. \( D_p \equiv D_c - D_{vdw}/\sqrt{2} \) is the pore diameter used for gas transport.

**Gases** (kinetic diameter [Å], molecular weight [g/mol]): He (2.6, 4.00), H\(_2\O\) (2.65, 18.02), Ne (2.75, 20.18), H\(_2\) (2.89, 2.02), NO (3.17, 30.01), CO\(_2\) (3.3, 44.01), Ar (3.4, 39.948), O\(_2\) (3.46, 32.00), H\(_2\)S (3.6, 34.08), SO\(_2\) (3.6, 64.07), Kr (3.6, 83.80), N\(_2\) (3.64, 28.01), CO (3.76, 28.01), CH\(_4\) (3.8, 16.04), Xe (3.96, 131.29), SF\(_6\) (5.5, 146.06) \(^{390}\).
While developing these novel membranes, it is important to consider their scalability from the laboratory to industrial systems. Industrial gas separation plants typically use membranes that have areas of 1000 to 500,000 m$^2$, last for 3 to 5 years, and cost less than 50 USD/m$^2$.2

1.1 Gas transport in membranes

Gas separation membranes are generally classified as dense or porous. Dense membranes operate by a solution-diffusion mechanism in which bulk gas on the high pressure side is dissolved into the membrane, diffuses through the material, and emerges on the low pressure side (Fig. 1-1).2,4,5,7–11 Selectivity results from differences in gas solubility ($s$) and diffusivity ($\kappa$) in the membrane ($Q_A/Q_B \approx (\kappa_A/\kappa_B)(s_A/s_B)$, where subscripts A and B correspond to different gases).

Porous membranes have defined passages throughout the membrane.3 These include membranes with pores patterned into the material as well as inherently porous structures. When the pore diameter is smaller than approximately three times the kinetic diameters of the gas molecules, gas transport is in the molecular sieving regime.4 The pores are sufficiently small that

![Figure 1-1. Simple membrane gas transport regimes. Here, $Q$ is permeance, $D$ is diffusivity, $S$ is solubility, $m$ is molecular mass, and $\mu$ is viscosity.](image-url)
the flow of larger gas molecules is strongly impeded compared to smaller gas molecules, due to size restriction, resulting in high selectivity.

For membranes with pores larger than a few kinetic diameters but still much smaller than the mean free path in the gas, gas flow is in the Knudsen diffusion regime.\(^4,\^{12}\) Both the smaller and larger gas molecules are all able to flow in the membrane pores at high rates. Lighter molecules have higher permeances since they move at higher average speeds than heavier molecules \((Q_A/Q_B \approx \sqrt{M_B/M_A})\).

As the pore size is increased further towards the micron-scale, the transport mechanism transitions from Knudsen diffusion to Poiseuille flow.\(^{13}\) In this limit, transport rates are dominated by viscosity. Single species permeance measurements are inversely proportional to viscosity \((Q_A/Q_B \approx \mu_B/\mu_A)\).

In general, since the rate of diffusion is inversely proportional to a characteristic membrane thickness, thin active layers are desirable.

### 1.2 Membrane materials and structures

Currently, all commercial gas separation membranes are polymeric solution-diffusion membranes, made from materials such as polyimide, cellulose acetate, and polysulfone.\(^2\) In these, diffusivity is related to the material structure;\(^4,\^{7,\,10,\,14}\) more tightly packed or highly cross-linked molecules tend to provide greater restriction to gas molecule motion in the material. Since the diffusivities of all gas species are affected by the material structure, choosing a more permeable material typically produces lower selectivity.\(^4,\,5\) This leads to an observed upper bound in the membrane permeance-selectivity relation (Fig. 1-2). This bound has been quantified for several common gas combinations and is referred to as the Robeson limit.\(^4,\,5\) Surface modifications and
mixed matrix structures can further enhance the performance of membranes above this limit.\textsuperscript{4,8,10,15–17}

Dense metallic membranes, often made from palladium alloys, are an extreme case of solution-diffusion membranes in which the tight crystal lattice makes it more favorable for hydrogen to dissociate before dissolving and diffusing through the membrane.\textsuperscript{15} This results in low permeance but high selectivity.

Porous molecular sieving membranes include carbon molecular sieves (CMSs), inorganic molecular sieves such as zeolites and metal organic frameworks (MOFs), and very high free volume polymers.\textsuperscript{18,19} Zeolites are nanoporous aluminosilicate minerals, which have a crystal structure with well-defined pores resulting in high surface area. MOFs have similar nanoporous structures created by coordination bonding between organic molecules and metal ions or clusters. CMSs are made by carbonization of MOFs or zeolites. It should be noted that “CMS” is also sometimes used to describe ultra-microporous carbon used for gas adsorption; this material is formed by pyrolysis of carbon precursors and has larger pores and very high surface area. Zeolites,

![Figure 1-2. Polymer membrane performance compared to the predicted performance of graphene. Polymer membrane data from Ref. 4. Graphene potential based on Refs. 33,59.](image-url)
MOFs, and CMSs have highly structured pores (Fig. 1-3). In contrast, very high free volume polymers, such as PTMSP (poly[1-(trimethylsilyl)-1-propyne]), have unstructured pores, still with a size similar to gas molecule diameters. Surface diffusion of adsorbed molecules within the pores of molecular sieves can be significant and selectivity can result from differences in adsorption affinities.

Membranes with patterned pores larger than 5 nm are also available for particle filtration. These include polymer track etched membranes (PCTEM) and anodic aluminum oxide (AAO) membranes. Knudsen selectivity is possible at the smaller end of the pore size range available for these membranes.

Figure 1-3. Membrane structure-thickness map. Image sources: polymer solution-diffusion membranes (reprinted from Ref. 131, with permission from Elsevier); carbon molecular sieves (reproduced in part from Ref. 132 with permission of The Royal Society of Chemistry); carbon nanotube (from Ref. 25, reprinted with permission from the American Association for the Advancement of Science); anodic alumina (from Ref. 133 © IOP Publishing. Reproduced with permission. All rights reserved); graphene oxide (from Ref. 134, reprinted with permission from the American Association for the Advancement of Science); metal organic framework & zeolite (reproduced from Ref. 135 with permission of The Royal Society of Chemistry); carbon nanomembrane (Reprinted with permission from Ref. 136. Copyright 2013 American Chemical Society); and graphene (reprinted by permission from Macmillan Publishers Ltd: Ref. 137, copyright 2012).
Other novel carbon-based membrane structures are currently being researched. These include carbon nanotube membranes (CNT),\textsuperscript{25-27} graphene oxide (GO) membranes,\textsuperscript{28,29} carbon nanomembranes (CNMs),\textsuperscript{30} and graphene membranes.\textsuperscript{31-34} The motivation behind such membranes is the potential to produce precisely controllable pore structures, so that selectivity can be maintained, in ultra-thin membranes, resulting in high permeance (Fig. 1-3).

CNTs are hollow cylinders of carbon that can be arrayed in parallel in a material such as epoxy to form a CNT membrane.\textsuperscript{25-27} Micron-scale membrane thicknesses with CNT diameters as small as 2 nm can be achieved. These membranes have high gas permeance and well defined pores.

Graphene oxide flakes are two dimensional, micron-scale structures containing carbon, oxygen, and hydrogen.\textsuperscript{28,29} These flakes can be assembled into a membrane by vacuum filtration or spin coating, with thickness ranging from less than 2 nm to microns. The primary gas transport pathway through these membranes is believed to be interlayer transport between GO flakes.\textsuperscript{28} Selectivity can result from differences in adsorption affinity within these spaces, possibly resulting from gas molecule interactions with epoxy, hydroxyl, or carboxyl groups on the GO flakes. These membranes show strong interaction with CO\textsubscript{2}. GO membranes have been prepared that selectively reject CO\textsubscript{2}, with H\textsubscript{2} / CO\textsubscript{2} selectivities of 3400.\textsuperscript{29} GO membranes have also been prepared that selectively permeate CO\textsubscript{2}.\textsuperscript{29}

CNMs are prepared by electron-radiation-induced cross-linking of self-assembled monolayers.\textsuperscript{30} This forms periodic structures with well-defined pores in layers as thin as 1 nm. Creating pores small enough for molecular sieving of gas molecules in these membranes remains a challenge.
1.3 Graphene membranes

Graphene, single atom thick carbon arranged in a two dimensional sheet, is a potential membrane material at the ultimate limit of thinness (Fig. 1-3). Graphene is impermeable to gases in its pristine state,\textsuperscript{31} can support sub-nanometer pores for molecular sieving,\textsuperscript{32,33} and will pose minimal resistance to gas flow by virtue of its atomic thickness.\textsuperscript{32,33} This gives nanoporous graphene the potential to surpass current membrane permeance and selectivity limits.\textsuperscript{31,32}

The state-of-the-art in graphene membranes for gas separation is reviewed in Ch. 2. The most significant accomplishments to date are (1) the experimental demonstration by Koenig et al.\textsuperscript{34} of molecular sieving through a single nanopore in mechanically exfoliated two-layer graphene, with $\text{H}_2 / \text{CH}_4$ selectivity exceeding 10\textsuperscript{4}, and (2) achieving near Knudsen selectivity with high permeance through a membrane with $10^6$ patterned 7.6 nm pores in two-layer graphene by Celebi et al.\textsuperscript{12} However, fabricating graphene membranes for gas separation applications will require a larger array of sub-nanometer pores to simultaneously achieve high permeance and high selectivity. Accomplishing this requires overcoming two main challenges: material defects and nanopore size variation.

Large areas of graphene are known to contain defects in the nanometer size range (Fig. 1-4).\textsuperscript{35} Because graphene is atomically thin, these defects can create non-selective leakage pathways for gas molecules. These defects can compromise membrane performance, and therefore need to be addressed.

While single pores in the molecular sieving size range can be produced,\textsuperscript{34} and arrays of large pores can be patterned,\textsuperscript{12} methods are needed to create a large array of pores in the molecular
sieving size range. The pore size distribution will determine the gas pairs that can be separated and the overall selectivity. The pore density will determine membrane permeance.

Figure 1-4. Intrinsic defects in large area CVD graphene (scanning electron microscope images reprinted with permission from Ref. 35. Copyright 2012 American Chemical Society).
1.4 Thesis aims

The overall objective of this research is to develop macroscopic graphene membranes for gas separation. Towards this goal, this thesis focuses on the following aims:

**Aim 1.** Investigate gas transport through intrinsic defects in single-layer and multi-layer graphene membranes;

**Aim 2.** Develop graphene membrane permeance models and apply them to delineate the parameter space for the design of selectively permeable membranes; and

**Aim 3.** Fabricate defect-tolerant nanoporous graphene membranes and demonstrate high-flux gas separation.

Background and prior work on graphene membranes for gas separation is detailed in Ch. 2. The inherent permeance of single and multi-layer graphene is investigated in Ch. 3 (aim 1). A model for gas transport through macroscopic areas of graphene is developed and applied to selective membrane design in Ch. 4 and 5 (aim 2). Membrane fabrication methods to achieve selective transport are developed in Ch. 6-8 (aim 3). Membrane performance is also characterized and analyzed in Ch. 8.
Chapter 2

Graphene membrane background

Bunch et al.\textsuperscript{31} experimentally demonstrated the impermeability of single-layer graphene to gases including helium. In their experiment, the change in deflection of pristine mechanically exfoliated graphene suspended over a pressurized silica microcavity was measured to determine the leakage rate (Fig. 2-1a,b). They showed that the measured leakage could be accounted for by diffusion through the silica substrate, with negligible contribution coming from flow between the graphene and substrate or due to quantum tunneling through the graphene lattice. The impermeability of pristine graphene in combination with the atomic thickness of the material led Bunch et al.\textsuperscript{31} to propose graphene as a membrane material. Subsequent simulations quantified the potentially high permeance and selectivity by molecular sieving through graphene.\textsuperscript{36-38}

2.1 Theoretical gas transport work

A large number of simulations have since been performed, predicting the gas permeance and selectivity of various gas species and nanopore structures. There are two general approaches
used to compute gas permeance and selectivity of graphene nanopores: (1) the energy barrier method and (2) molecular dynamics simulations.

In the first approach, the energy barrier to crossing the pore is calculated for the gas molecules of interest (Fig. 2-2, 2-1c) and used in an Arrhenius rate law to estimate selectivity, \( S \).

\[
S = \frac{e^{-E_1/k_BT}}{e^{-E_2/k_BT}} \tag{2-1}
\]

where \( S \) is the selectivity, \( k_B \) is Boltzmann's constant, \( T \) is the temperature, and \( E_1 \) and \( E_2 \) are the energy barriers for the two molecules to cross the pore. In some studies, permeation rates are also estimated from the energy barrier following the method of Schrier. In this method, the transmission probability is calculated as the fraction of incident gas molecules with Maxwell-Boltzmann velocity distribution that have sufficient velocity normal to the pore to overcome the energy barrier. The single component Maxwell-Boltzmann velocity distribution is

\[
f(v_x) = \frac{m}{\sqrt{2\pi k_B T}} e^{-mv_x^2/(2k_BT)} \tag{2-2}
\]
where \( f(v_x) \) is the probability that a molecule has x-component of velocity, \( v_x \). The fraction of molecules with speed greater than \( v_{x,\text{min}} = \sqrt{2E/m} \) is therefore,

\[
\frac{J}{J_{\text{ideal gas}}} = \frac{1}{2} \text{erfc} \left( \sqrt{\frac{E}{k_BT}} \right)
\]

(2-3)

where \( E \) is the energy barrier (for \( E/k_BT \gg 1 \), \( J/J_{\text{ideal gas}} \approx \frac{1}{2} \sqrt{k_BT/\pi E e^{-E/k_BT}} \)).

Note that Eq. 2-1 and 2-3 give only order of magnitude approximations for permeance and selectivity from calculated energy barriers. The details of transport are not simulated in either calculation. Notice also that the selectivity from Eq. 2-3 for \( E/k_BT \gg 1 \) is \( S = J_1/J_2 \approx \sqrt{m_2E_2/m_1E_1} e^{-E_1/k_BT}/e^{-E_2/k_BT} \). Comparing to Eq. 2-1, it is apparent that the order one pre-factor to the exponential terms is neglected. Since both Eq. 2-1 and 2-3 neglect the details of gas transport, and reported selectivities are often very large (\( S \gg 1 \)), neglecting such factors is reasonable.

Figure 2-2. Example of a potential energy profile across a graphene nanopore. a, Definition of z-axis, which molecule traverses. b, Selected pore geometry. c, Corresponding potential energy profiles for hydrogen and nitrogen computed using a Lennard Jones potential.
Density functional theory (DFT) is commonly used to calculate the energy barrier,\textsuperscript{32,37,42–}56 although, some studies use a post-Hartree-Fock method.\textsuperscript{38,39} Most often, the position and orientation of the gas molecules are constrained in calculating the energy profile and barrier heights, however, some studies perform more involved transition state searches.\textsuperscript{38,39,48,50,52,56}

In the second approach, the gas dynamics are simulated to calculate the number of molecules crossing the nanopore per unit time (Fig. 2-1d, 2-3).\textsuperscript{32,36,40,41,44,46,57–73} Selectivities are then calculated as the ratio of computed permeances. Classical molecular dynamics (MD) is used almost exclusively for this approach, although first principles molecular dynamics results have also been reported.\textsuperscript{32}

Due to restrictions on the total simulated time, MD has been limited to predicting selectivities of less than 100 to 1000,\textsuperscript{32,36,40,41,44,46,57–73} with the high end achievable only at elevated pressures. Often, no molecule crossings are observed if the nanopores are more selective than this.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-3.png}
\caption{Comparison of single pore transport measurements by Koenig et al.\textsuperscript{33} to molecular dynamics simulation results of Au\textsuperscript{59} for various pore sizes. Shaded regions show estimated uncertainty in molecular dynamics simulation results. Measurements are shown for pores with estimated molecular size cut-offs of 3.4 and 4.9 Å. Simulated pore geometries also shown (reproduced from Ref. 59).}
\end{figure}
DFT predictions of selectivity of up to $10^{78}$ has been reported. However, the precise permeance and selectivity, which would include prefactors to the Arrhenius rate law for different gases, are not obtained by DFT calculations. For these reasons, it is common to use DFT to estimate selectivity and MD to estimate permeance.

The majority of simulations fix the two-dimensional lattice when computing the energy barrier or simulating the molecular dynamics. However, some studies have allowed for lattice deformations. In DFT calculations, lattice deformation due to the presence of a gas molecule has been accounted for by re-optimizing the in-plane lattice structure when traversing a gas molecule across the pore to obtain potential energy profiles. In molecular dynamics simulations, the AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential has sometimes been used, allowing for deformation and thermal fluctuations in the graphene lattice. By both methods, comparisons with the corresponding results for a fixed lattice indicate that neglecting lattice motion can yield selectivities that are several orders of magnitude too high.

### 2.1.1 Theoretical predictions

Simulations have been performed on nanopores with diameters up to 11 Å, with various pore edge groups (C, H, N, O, F, and various atomic species). Although simulations have largely focused on graphene, a variety of gas species (CH₄, CO₂, CO, H₂S, Ar, Ne, NH₃, H₂O, alkanes, 3He, 4He, UF₆, UF₆, D₂, Kr, Xe, Rn, and various atomic species) have been studied.
simulations have also been performed for various other two-dimensional materials with nanopores suitable for molecular sieving, including porous graphene with various modifications,\textsuperscript{38,40,46,47,54,60,67,69} graphdiyne,\textsuperscript{43,51,57} graphyne,\textsuperscript{43} polypheneylene,\textsuperscript{39,53,74} porphyrin,\textsuperscript{41} silicene,\textsuperscript{50} and hexagonal boron nitride.\textsuperscript{44} This general class of membranes will be referred to as nanoporous atomically thin membranes (NATMs). Figure 2-4 summarizes all of the available simulation data on gas transport through nanopores in atomically thin materials.\textsuperscript{32,36–38,40,41,43–46,48–60,62,63,65,67–73} Appendix A details how these data were complied.

For the majority (~75%) of simulated pores the permeation coefficient of the most permeable molecule is in the range $10^{-23}$–$10^{-19}$ mol/s-Pa. For a pore density of $10^{12}$ cm$^{-2}$, this corresponds to a membrane permeance of $10^{-7}$–$10^{-3}$ mol/m$^2$-s-Pa ($10^2$–$10^6$ GPU). However, some simulations involve pore densities of up to $8.5 \times 10^{14}$ cm$^{-2}$, resulting in permeances of up to $10^{-1}$ mol/m$^2$-s-Pa ($10^8$ GPU).

### 2.1.2 Transport pathways

Simulations have provided insights into the gas transport pathways across graphene nanopores.\textsuperscript{75,76} Several separation mechanisms have been reported. Specifically, selectivities are affected by differences in molecule size,\textsuperscript{36,55,57–60,62,63,65–73,75,76} mass,\textsuperscript{70} adsorption affinity,\textsuperscript{45,58,66–70,72,74,76,77} interaction with functional groups on the pore rim,\textsuperscript{32,37,40,41,44–47,49,52,54,62,63,65,67,68,71,73,74} configurational entropy,\textsuperscript{69} and tunneling rates.\textsuperscript{38,39,42,47–49,52} These are described below.

Size-sieving occurs when the effective pore size significantly limits the permeance of the larger molecules compared to the smaller molecules.\textsuperscript{36,55,57–60,62,63,65–73,75,76} Compared to typical kinetic energies of the gas molecule, the barrier height for smaller molecules is low whereas that for larger molecules is high.
Figure 2-4. Predicted and measured performance of graphene nanopores. 32,36-38,40,41,43-46,48-60,62,63,65,67-73
a, Effective pore area (Box 1-1). b, Selectivity. Details on transport regime models are presented in Section 2.3. The procedure for extracting simulation and experimental data to construct these plots is detailed in Appendix A.
Partial charges on functional groups on the nanopore edge can also interact with the gas molecules, affecting permeance.\textsuperscript{32,36-41,43-47,49,51-54,56,57,60,62,63,65,67,68,71,73,74} These interactions have been found to be particularly important in the transport of molecules with polar bonds.\textsuperscript{65,67,68}

Differences in molecule mass give rise to separation because lighter molecules move at higher average speeds than heavier molecules, resulting in a higher flux of the lighter molecules across the nanopore. Mass differences result in selectivity even for nanopores too large for size-sieving.\textsuperscript{70}

In addition to molecules approaching the nanopores from the bulk gas, molecules also tend to adsorb on graphene and diffuse in two-dimensions towards the pore (Fig. 2-5c).\textsuperscript{45,58,66-70,72,74,76,77} This can increase the rate of attempted molecule crossings, enhancing permeance. The significant absorption of gas molecules on graphene is illustrated in Fig. 2-6, in which the molecular dynamics simulation results of Au\textsuperscript{59} have been processed to show adsorption layers on a graphene membrane. Simulations show that permeance is enhanced in the order SO\textsubscript{2}\textsuperscript{74} > CO\textsubscript{2}\textsuperscript{67,68,74} > CH\textsubscript{4}\textsuperscript{67,70,74} > H\textsubscript{2}O\textsuperscript{74} > N\textsubscript{2}\textsuperscript{58,67,68,70,72,74} & O\textsubscript{2}\textsuperscript{67,74} > H\textsubscript{2}\textsuperscript{58,70,72} > He\textsuperscript{70}, and H\textsubscript{2}S\textsuperscript{74} > CH\textsubscript{4}, and paraffins > olefins\textsuperscript{69}. It has further been suggested that molecules in a mixture with higher adsorption affinity will tend to displace other molecules from the surface, reducing that gas’s permeance.\textsuperscript{72}

For long hydrocarbon chains, it has been shown that separation can result from differences in configurational entropy in the vicinity of the pore.\textsuperscript{69} This can result in selective transport of shorter hydrocarbon molecules compared to longer ones\textsuperscript{69}

At low temperatures, where the energy barrier is very high compared to typical kinetic energies of the gas molecules, rates of quantum tunneling across graphene nanopores can be
Figure 2-5. Prevalent transport mechanisms through graphene nanopores. Illustration of the a, activated and b, steric transport regimes as well as of the c, adsorption pathway. d, Steric regime calculation of the fraction of ideal gas flux permeating the pore for a given ratio of molecule to pore diameter. The data were generated from Monte Carlo simulations discussed in Section 2.3.1. The equation for ideal gas effusion through an area accounts for the rate of incidence of the center of mass of gas molecules on that area. However, for small pore areas, the non-zero size of the gas molecule colliding with the pore rim reduces the flux of molecules through the pore. The fraction of the incident flux on area $\pi D_p^2/4$ that passes through the pore is plotted against molecule size in this panel. Plot shows simulation results (markers) and an interpolating curve.

significantly higher than classical permeation rates.$^{39,42,47-49,52}$ This has been proposed as a method of separating helium isotopes.$^{48}$

2.2 Experimental gas transport work

Koenig et al.$^{33}$ successfully demonstrated molecular-sieving through graphene nanopores. They created nanopores in bi-layer graphene suspended over microcavities by ultraviolet induced oxidative etching. They measured gas permeance based on changes in membrane deflection or
Figure 2-6. Adsorption of gas molecules, obtained from the molecular dynamics simulations of Au\textsuperscript{59}. a, Simulation domain of Au\textsuperscript{59}. b,c, Number of adsorbed molecules within 1 Å horizontal slices of the total 1600 molecules per gas species divided between 16 replicate simulations. Pore geometry inset (pore geometry images reproduced from Ref. 59).

Resonant frequency over the pressurized cavity. The permeance of H\textsubscript{2} and CO\textsubscript{2} increased by two orders of magnitude after etching while the permeance of the larger Ar, N\textsubscript{2}, and CH\textsubscript{4} molecules was unchanged, demonstrating molecular-sieving with a pore size of approximately 3.4 Å (Fig. 2-7a). The maximum permeances they report were in the range $5 \times 10^{-23}$ to $10^{-21}$ mol/s-Pa, with selectivities of greater than $10^4$. On similarly fabricated single-layer porous graphene membranes, Wang et al.\textsuperscript{78} report gas permeance in the range $10^{-23}$ to $10^{-22}$ mol/s-Pa. Predictions from simulations are consistent with these measurements (Fig. 2-3, 2-4).

Wang et al.\textsuperscript{78} further observed unexpectedly high permeances of CO\textsubscript{2} and N\textsubscript{2}O compared to He, Ne, H\textsubscript{2}, and Ar. They attributed this to interactions between functional groups on the pore edge and polar groups, which have been found to significantly affect transport rates for such gas molecules in simulations.\textsuperscript{65,67,68} In this system, Wang et al.\textsuperscript{78} discovered stochastic switching
behavior in which the permeance of the nanopore changes discretely due to changes in pore configuration. Permeance changes of approximately an order of magnitude were recorded, with switching time scales ranging from minutes to hours. By laser heating a graphene membrane with a nanopore covered in gold nanoclusters, Wang et al. were able to concentrate the particles over the pore and reduce gas permeance five-fold. This demonstrates the possibility of graphene nanopore flow control.

Larger nanopores cannot provide size-sieving but still have modest selectivities due to the mass dependence of average molecule speeds. The permeance of such pores is still very high owing to the atomic thickness of the membrane. Celebi et al. fabricated membranes with $10^3$-$10^6$ pores of 7.6-1000 nm diameter in two-layer graphene by focused ion beam drilling (Fig. 2-7b). By this
method they produced a membrane with 4.0% porosity having measured H₂/CO₂ selectivity near the Knudsen value (4.7) and permeance (~10⁻² mol/m²-s-Pa) more than three orders of magnitude higher than existing gas separation membranes with similar selectivity.

### 2.3 Modeling gas transport in nanoporous graphene

The available data for gas transport through graphene nanopores can be further understood using a simple scaling model. When the gas molecule is relatively large compared to the pore, transport is treated as being limited by an activation barrier, whereas when the gas molecule is relatively small compared to the pore, transport is treated as being limited by steric hindrance. These regimes are both described below, with pore size parameters defined in Fig. 2-8. This model captures the scaling observed from experiments and simulations (Fig. 2-4).

#### 2.3.1 Steric regime model

Relatively large nanopores are approximated as behaving as open areas in a rigid barrier. The gas molecules are treated as rigid spheres with the kinetic diameter of that gas and a Maxwell-Boltzmann velocity distribution. Gas molecules incident on the membrane from the bulk pass
through if no part of the sphere intersects the rigid barrier along the molecule’s trajectory (Fig. 2-5b). This is the model proposed by Sun et al. The pore is approximated as being circular with diameter \( D_p = \sqrt{4A_p/\pi} \), where \( A_p \) is the pore area. As described in more detail in Section A.1, the pore area \( (A_p) \) is defined here as the in-plane open area within the pore when atoms in the NATM are taken to be spheres with diameter equal to their van der Waals diameter divided by \( \sqrt{2} \) (Fig. 2-8a,b). The \( \sqrt{2} \) factor gives an approximate collision cross-section for the pore rim atoms. Although pore area definitions vary in the literature, the data in Fig. 2-4 have been converted to this definition.

A Monte Carlo simulation is used to compute the fraction of gas molecules incident on the open area that pass through as a function of \( D_m/D_p \), where \( D_m \) denotes the molecule kinetic diameter. The point in the plane of the pore that the center of the sphere crosses is selected randomly within the pore area. The incident angle of the molecule is also selected randomly, however, the sample distribution accounts for the fact that molecules approach with greater frequency from steeper angles \( (P(\theta) = \sin 2\theta, \) where \( P(\theta) \) is the probability density of the incident molecule approaching the pore at angle \( \theta \) from the normal to the graphene plane). As the sphere traverses the pore it sweeps out an elliptical contact area with the plane of the pore. Example in-plane areas are shown in Fig. 2-5b in green for one molecule and red for another. A crossing is counted if this area is completely within the circular pore. For example, in Fig. 2-5b, the molecule sweeping out the green area is counted as crossing the pore whereas the molecule sweeping out the red area is rejected. After many samples, the fraction of molecules that cross the pore for a specified \( D_m/D_p \) is computed as,

\[
\frac{J}{J_{\text{ideal gas}}} = \frac{\text{Number of crossings}}{\text{Number of incident molecules}}
\]  

(2-4)
This calculation is described further by Sun et al.\textsuperscript{70}

This model neglects some important effects. Notably, it neglects adsorptive flux, geometric details of the pore and gas molecules, three dimensionality of the pore, and non-hard sphere interactions between the membrane and the gas molecules.

### 2.3.2 Activated regime model

Nanopores with relatively small effective open areas could provide almost complete steric exclusion if the molecules were rigid. However, it is important to consider that the pore rim and gas molecules are not rigid. The intermolecular potential allows the centers of these molecules to be closer than a hard sphere potential would permit. However, the repulsive nature of the potential at close range means that there is an energy barrier to the gas molecule center being close enough to the pore rim molecule centers to cross through the pore.

In this model, the energy barrier for a molecule to pass through a pore is estimated using a Lennard-Jones potential to describe the molecule-pore interactions. The pore is approximated as a circular aperture of diameter $D_c$ with a continuous linear density of pore rim atoms (\textit{i.e.}, a torus, Fig. 2-8c).

In the Lennard-Jones potential, the interaction energy depends on the center-to-center distance of atoms. The appropriate interatomic distance in this model is $D_c/2$, the distance from a gas molecule at the center of the pore to the center of a carbon atom on the pore rim (Fig. 2-8c). However, pore diameter has been defined based on the steric model as $D_p = \sqrt{4A_p/\pi}$ (Fig. 2-8b). This estimate, as shown in Fig. 2-8b, is based on an effective pore area that excludes the effective collision cross section of carbon atoms in the graphene lattice. $D_c$ can therefore be approximately calculated from $D_p$ as follows: $D_c = D_p + D_{vdw}/\sqrt{2}$. 

36
### Table 2-1. Lennard-Jones parameters used in permeance scaling model.\(^{129}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C-C</th>
<th>H(_2)-H(_2)</th>
<th>CH(_4)-CH(_4)</th>
<th>C-H(_2)</th>
<th>C-CH(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma \text{ [Å]})</td>
<td>3.385</td>
<td>2.827</td>
<td>3.758</td>
<td>3.106</td>
<td>3.5715</td>
</tr>
<tr>
<td>(\varepsilon \text{ [eV/K]})</td>
<td>(2.637 \times 10^{-3})</td>
<td>(5.144 \times 10^{-3})</td>
<td>(12.805 \times 10^{-3})</td>
<td>(3.683 \times 10^{-3})</td>
<td>(5.811 \times 10^{-3})</td>
</tr>
</tbody>
</table>

The energy barrier encountered by a molecule at the center of this pore is approximately given by,

\[
E \sim \frac{\pi D_c}{a} \left( \frac{\sigma}{D_c/2} \right)^{12} - \left( \frac{\sigma}{D_c/2} \right)^6
\]  

(2-5)

The \(\pi D_c/a\) prefactor approximates the number of carbon atoms on the rim of a pore of that size, where \(a\) is the distance between adjacent atoms (in Fig. 2-4, \(a = 1.42\ \text{Å}, \) the bond length in graphene). Lorentz-Berthelot mixing rules were used to compute the \(\sigma\) and \(\varepsilon\) parameters from those for carbon and equivalent single point interaction models for the gas molecules. The values used are provided in Table 2-1.

From this energy barrier, the transmission probability is calculated by the method of Schrier\(^{38}\) discussed above,

\[
\frac{J}{J_{\text{ideal gas}}} = \frac{A_{\text{eff}}}{A_p} = \frac{1}{2} \text{erfc} \left( \frac{E}{\sqrt{k_B T}} \right)
\]

(2-6)

This gives the transmission probability at the center of the pore.

The activated regime model also neglects some effects. Notably, it neglects adsorptive flux and the detailed geometry, charge, and flexibility of the bonds in the pore and gas molecule.
2.3.3 Combined model

The steric regime model does not apply to very small pore sizes. For example, it predicts zero transmission probability as \(D_p - D_m\) goes to zero. However, since the pore is not made of perfectly hard molecules, there is still a nonzero probability of transmission in this case. At the other extreme, the activated regime model does not apply for relatively large pore sizes. When the energy barrier is zero or negative, it predicts that there is no obstruction to crossing the pore. The effective area needs to be adjusted by a factor accounting for the geometric hindrance of the pore rim in this case.

The steric and activated regime models are combined into a single continuous pore permeance coefficient versus pore size curve for each gas molecule in a simple way. The steric model is used for pore diameters down to the size at which the activated model predicts a lower permeance, and then that model is used for all smaller pore sizes. This change-over point depends on the gas molecule, allowing some pores to operate in the steric regime for smaller gas molecules and in the activated regime for larger gas molecules. This is the ideal operation for high permeance and high selectivity.

Both regime models give transmission probabilities. To convert to pore permeance coefficient, they are multiplied by the ideal gas flux. To obtain the pore permeation coefficient, they need to be further multiplied by an appropriate pore area. In the steric regime, this area is \(A_p = \pi D_p^2 / 4\), by the way the steric regime transmission coefficient was defined. In the activated regime, the appropriate area is less apparent since the transmission probability is calculated at a single point within the pore. Here, the same area \((A_p)\) is used as in the steric regime. It should be noted that this may result in an over-estimate of the pore permeance and membrane permeance.
2.4 Defects

Fabricating graphene membranes with large areas has relied on chemical vapor deposited (CVD) graphene as opposed to more pristine but smaller area mechanically exfoliated graphene.\textsuperscript{12,28,81} However, intrinsic nanometer-scale defects in CVD graphene produce unwanted, low-selectivity gas leakage through the membrane.\textsuperscript{12,28,81} This can compromise membrane performance.

Stacking multiple layers of CVD graphene is the main method that has been used to enhance the gas barrier properties of graphene.\textsuperscript{12,28,81} The gas transport experiments of Koenig et al.\textsuperscript{33} and Celebi et al.\textsuperscript{12} both used two-layer graphene. In stacking five layers of graphene, Kim et al.\textsuperscript{28} were able to reduce the inherent gas permeance of $O_2$ by 25-fold while increasing the $O_2/N_2$ selectivity from 1.5 to 6. They proposed that this selectivity and the remaining permeance resulted from gas diffusion through defects in the graphene and through the space between graphene layers, similar to transport in GO membranes. Residue from the sacrificial polymer layer used during graphene transfer may create a large interlayer spacing allowing such transport.

2.5 Nanopore creation methods

Various methods have been used to create pores in graphene. However, creating a high density of pores with a narrow size distribution over a large area remains challenging.

Koenig et al.\textsuperscript{33} created a gas molecule size selective nanopore in graphene by etching in an ultraviolet (UV) ozone cleaner. Gas permeation measurements showed that gas molecules smaller than 3.4 Å could pass through one membrane and smaller than 4.9 Å could pass through another
membrane. This gives an indication of the pore size. However, the experiment did not permit imaging of the pores.

Over larger areas, Surwade et al.\textsuperscript{82} used oxygen plasma etching (20 W, < 6 s exposure) to create nanopore densities of $10^{12}$ cm\textsuperscript{-2} (Fig. 2-9a,b). High water flux desalination across these membranes by an evaporative mechanism was demonstrated by transport experiments in which the membrane was wetted on one side.\textsuperscript{82,83} The created pore size distribution is not available.

O’Hern et al.\textsuperscript{84} demonstrated that $10^{12}$-$10^{13}$ cm\textsuperscript{-2} densities of sub-nanometer pores can be created in graphene by gallium ion bombardment (8 kV, $6 \times 10^{12}$ ion/cm\textsuperscript{2}, 52° or 1 kV, $7 \times 10^{13}$ ion/cm\textsuperscript{2}, 0°)\textsuperscript{84,85} to nucleate defects followed by potassium permanganate etching (1.875 mM in 6.25% sulfuric acid, < 2 h exposure) to enlarge these sites (Fig. 2-9g-j). The pore size distribution (Fig. 2-9j) shows that while sub-nanometer pores are produced, the size distribution has a spread of approximately 0.5 nm. This distribution could be a limitation for gas separation, where sizes for important applications can differ by less than 0.05 nm (Box 1-1).

Russo et al.\textsuperscript{86} similarly used argon ion irradiation (3 kV, $1 \times 10^{13}$ ion/cm\textsuperscript{2}) to nucleate nanopores followed by electron irradiation (80 kV, < $2 \times 10^{23}$ e\textsuperscript{-}/cm\textsuperscript{2}) to enlarge the pores (Fig. 2-9k-p). They demonstrated precise control over pore size in the 1 to 4 nm range by controlling the electron exposure density (Fig. 2-9p) as well as the size distribution created at a set electron exposure density (Fig. 2-9n). However, the electron exposure densities employed for the 100 nm diameter area treated in these experiments may be prohibitively high for perforating centimeter-scale areas.

Arrays of larger pores, from 7.6 nm to 1 μm, have been patterned in graphene using a focused ion beam, by Celebi et al.\textsuperscript{12} (Fig. 2-9c-e). Pores smaller than 10 nm were milled with a helium ion beam (30 kV, 16 pA, $6 \times 10^{-3}$ pA/nm\textsuperscript{2}), whereas larger pores were created with a gallium
ion beam (30 kV, 33 pA, 0.5-5×10⁻⁵ pA/nm²). They were able to produce 10³ to 10⁶ pores per membrane. However, these pores are not suitable for molecular sieving, as the sizes are much larger than the typical gas molecule kinetic diameters of 0.25 to 0.6 nm (Box 1-1).

Figure 2-9. Pore creation methods. a,b, Oxygen plasma etching, by Surwade et al.⁸² a, Sketch. b, Scanning transmission electron microscope image of created pores by 1.5 s plasma exposure (reprinted by permission from Macmillan Publishers Ltd: Ref. 82, copyright 2015). c-f, Focused ion beam patterning, by Celebi et al.¹² c, Sketch. d, Array of 7.6 nm pores patterned in graphene. e, Example 15 nm pore. f, Size distribution of patterned 7.6 nm pore array. (d-f from Ref. 12. Reprinted with permission from the American Association for the Advancement of Science). g-j, Gallium ion irradiation followed by potassium permanganate etching, by O’Hern et al.⁸⁴ g, Sketch. h,i, Example of pores created. j, pore size distribution for 25 minute etch (h-j reprinted with permission from Ref. 84. Copyright 2014 American Chemical Society). k-p, Argon ion irradiation followed by electron irradiation, by Russo et al.⁸⁶ k, Sketch. m, Example pore. n, pore size distribution created from 1×10¹⁵ ion/cm² bombardment and 9.7×10⁶ e⁻/Å² irradiation. p, Dependence of pore size on electron dosage (m,p reproduced from Ref. 86).
2.6 Graphene's potential

The first estimates of potential graphene membrane performance\textsuperscript{32} for $\text{H}_2/\text{CH}_4$ separation promised permeance values of $1\ \text{mol/m}^2\cdot\text{s-Pa}$ compared to $10^{-7} - 10^{-5}\ \text{mol/m}^2\cdot\text{s-Pa}$ for thin polymer membranes\textsuperscript{4} and selectivities of $10^8 - 10^{23}$ compared to $10 - 10^3$ for polymer membranes. From the experimental and theoretical work that has been performed since then, more realistic estimates of graphene membrane performance can be made. Figure 2-10 compares the performance of state of the art membrane technology to predictions for graphene membranes and other NATMs. These predictions are made based on single nanopore measurements and simulations assuming a pore density of $10^{12}\ \text{cm}^{-2}$, which has been achieved in experiments. For materials with inherent...
nanoporosity, the actual pore density of the material is used in the calculations. While the predicted permeance gains are far more modest than initially suggested, they still correspond to orders of magnitude of improvement for a given selectivity.

The key challenges in realizing these nanoporous graphene membranes for molecular sieving based gas separation are: (1) mitigating non-selective leakage sources in large area graphene and (2) generating a high density of small nanopores with a narrow size distribution over large areas. Further developments in membrane design and fabrication are needed to overcome these obstacles.
Chapter 3*

Inherent Permeance of Graphene

The imperfect quality of large areas of graphene presents a significant challenge in scaling single-layer graphene membranes to macroscopic sizes. Small areas of pristine graphene are impermeable even to helium, but due to the difficulty in isolating large areas of pristine graphene, macroscopic graphene membranes inherently have a non-zero permeance due to the presence of defects in the graphene. Gas leakage through defects in macroscopic graphene membranes can severely limit their selectivity and make separation impossible. To date, macroscopic area graphene-based gas separation has been demonstrated only in multi-layered membranes prepared from graphene oxide, where permeance is 3-4 orders of magnitude lower than that predicted by simulations across single-layer graphene membranes. Even in these multi-layer membranes, gas transport through defects can play a role in addition to interlayer transport. It is therefore critical to understand transport through defects in graphene and to develop strategies to mitigate non-selective leakage if the full potential of graphene membranes for gas separation is to be realized.

* Chapters 3-5 adapted with permission from Ref. 81. Copyright (2014) American Chemical Society.
In this chapter, the structure of single and few-layer macroscopic graphene membranes is investigated and their inherent permeance due to defects is measured. It is shown that independent stacking of two to five layers of graphene is a promising method for reducing the effects of defects while maintaining the nanometer-scale thickness of the graphene layer.

### 3.1 Gas permeance measurements

Gas flow rates through the graphene composite membrane were measured using the apparatus sketched in Fig. 3-1. The membrane was sealed between an upstream pressure line and a downstream reservoir, both initially evacuated. During measurements, the upstream line was continuously supplied with a single gas species at an absolute pressure of 1 atm by a regulated gas cylinder. A pressure transducer was used to measure the rate of pressure rise in the downstream reservoir, resulting in time traces such as those presented in Fig. 3-2b. The slope of the pressure-time line was used in an ideal gas law relation to determine the flow rate through the graphene membrane. Further details on the measurement equipment and procedure are provided in Appendix B.

![Figure 3-1. Schematic of membrane permeance measurement setup.](image-url)
Figure 3-2. Bare PCTEM flow rates. a, Illustration of gas molecule for which permeance was measured (helium, He; nitrogen, N₂; and sulfur hexafluoride, SF₆), with kinetic diameters indicated. b, Example pressure-time histories in the downstream reservoir, the slope of which is proportional to flow rate. c, Nitrogen flow rates through 1 μm diameter pore PCTEM at different upstream pressures. d,e, Gas permeance (d) and selectivity (e) measured on PCTEMs over a range of pore diameters.

3.2 Membrane synthesis

Graphene membranes were fabricated by transferring graphene grown on copper foil by chemical vapor deposition (CVD) to a PCTEM support using a direct transfer method developed previously (Fig. 3-3a). Graphene on copper foil (ACS Materials graphene was used for the experiments in this chapter) grown by chemical vapor deposition was first cut into approximately...
5 mm squares and the back sides of these pieces were etched for 5 min in ammonium persulfate (APS-100, Transene) to expose the copper and reduce the foil thickness. After rinsing the ammonium persulfate by floating on water baths, dipping in water to wash away curled up graphene, and air drying, the piece of graphene on copper foil was mechanically pressed onto a larger polyvinylpyrrolidone (PVP) free PCTEM (Sterlitech). The remaining copper foil was then completely removed by floating the stack on an ammonium persulfate solution under a 2 atm nitrogen atmosphere. The resulting composite membrane, comprised of a single layer of graphene on a PCTEM, was then rinsed in ethanol before air drying. Subsequent layers of graphene were transferred one-by-one by mechanically pressing graphene on copper foil onto a PCTEM onto which graphene had already been transferred, etching the copper away, rinsing, and drying.

PCTEMs were chosen as the porous support because they contain a high density of straight, well-defined pores with uniform sizes that can be tuned from 10 nm to over 10 μm. The porous support allows the graphene layer to be handled without damage. The series of parallel pore channels in the PCTEM also isolate small areas of graphene, such that the graphene composite membrane is effectively formed from numerous smaller graphene membranes arrayed in parallel. Flow through any defect in the graphene is restricted by the narrow channels in the PCTEM, which can potentially prevent leakage from dominating over the flow through intentionally created selective pores.

In addition, it was hypothesized that the effects of leakage may be further mitigated by independently stacking multiple layers of graphene on the porous support, so that defects in one layer are covered by another layer. To achieve this goal, the transfer process was repeated to create membranes with multiple independently stacked layers of graphene (Fig. 3-3a). In a multi-layer
Graphene membrane (Fig. 3-3b), individual layers of graphene can be distinguished by the successively darker areas over the white PCTEM.

Figure 3-3. Graphene composite membranes. a, Membrane fabrication process by direct transfer of graphene from copper foil to a polycarbonate track-etched membrane (PCTEM). The copper foil was etched using ammonium persulfate (APS). Multi-layer graphene composite membranes were fabricated by repeated application of the one layer transfer process. b, Photograph of a four-layer graphene composite membrane. Scale bar 5 mm. c,d, SEM images of a one-layer (c) and five-layer graphene membrane (d) with tears. Scale bars are 5 μm and 1 μm.
The direct transfer procedure outlined above was used to for 200 nm and 1.0 μm pore PVP-free PCTEMs used for the experiments in this chapter. Modifications to this procedure for smaller pore diameter PCTEMs are described in Section 7.2.1.

### 3.3 Characterizing membrane structure

Scanning electron microscope (SEM) images of the graphene membranes were obtained to understand the resulting structure with graphene on PCTEMs. SEM images were acquired with the JEOL 6320FV Field-Emission High-Resolution SEM at the MIT Center for Materials Science and Engineering. All images were obtained at an acceleration voltage of 5 kV in secondary electron imaging mode. Carbon tape was used to create a current path between the graphene and the microscope stage to reduce charging of the polycarbonate support material.

SEM images of a single layer of graphene (Fig. 3-3c) clearly show several polycarbonate pores with micrometer-scale tears in their graphene coverage. In contrast, SEM images of a five-layer graphene membrane (Fig. 3-3d) show a much smaller fraction of tears as compared to the single-layer membrane. The images clearly show that independently stacked graphene layers improve graphene coverage on the PCTEM.

Aberration corrected scanning transmission electron microscope (STEM) images of this graphene, show that, in addition to micrometer-scale tears in the membranes, the graphene also has intrinsic nanometer-scale defects (Fig. 3-4). Both of these scales of holes produce transport pathways for gas through the membrane. Although stacking graphene layers helps cover tears and defects in the membrane, there are places where tears or defects align, creating though holes in the membrane. Consequently, even multi-layer macroscopic graphene membranes are inherently permeable.
3.4 Inherent permeance of graphene

Transferring a single layer of graphene onto a PCTEM reduced the flow rate of helium through the PCTEM by approximately 60%, as seen in Fig. 3-5a,c. Since no selective pores were created in graphene, the residual 40% leakage represents helium flow through intrinsic defects and tears in the graphene. Next, helium flow rates through graphene membranes with one to five layers of graphene were examined, and observed to decrease exponentially as the number of graphene layers was increased (Fig. 3-5). By stacking multiple layers of graphene on a PCTEM, it was possible to produce a macroscopic graphene membrane with a 99% smaller permeance (i.e., only 1% leakage) compared to the bare support membrane. Furthermore, the apparent exponential decay of flow rates with increasing number of layers of graphene suggests that approximately the same fraction of polycarbonate pores are covered by graphene in each layer, and that the locations of the micrometer-scale tears in each layer are independent of those in the other layers.
3.5 Conclusions

A gas permeance measurement system was developed for graphene membranes, and used to measure the inherent permeance of single and multi-layer graphene. It was shown that leakage through graphene membranes decreases exponentially with increasing graphene layers. Imaging revealed that micrometer-scale tears and nanometer-scale intrinsic defects both contribute to the inherent permeance of these membranes.
Chapter 4

Graphene Permeance Modeling

In order to apply the knowledge of membrane structure and the inherent permeance of graphene to selective membrane design, a quantitative model for graphene permeance is desired. In this chapter, a gas transport model based on the determined membrane structure is developed to explain the experimentally measured inherent permeance of graphene. From this model, the separate contributions of micron-scale tears and nanometer-scale intrinsic defects to the inherent permeance of macroscopic graphene membranes are estimated. Furthermore, the possibility of gas transport between graphene layers is examined.

4.1 Resistance model

Since pristine graphene is impermeable to gases,\textsuperscript{31} it is assumed that the net permeance of macroscopic graphene membranes is a result of flow through micrometer-scale tears over the PCTEM pores, intrinsic nanometer-scale defects dispersed across areas of continuous graphene,\textsuperscript{35} and any intentionally created selective nanopores (Fig. 4-1).
Figure 4-1. Transport pathways considered in the graphene permeance model. Illustration of the change in tears and intrinsic defects over a, polycarbonate track-etched pores upon transferring b, one and c, two layers of graphene onto the PCTEM.
Micrometer-scale tears are accounted for by assuming that each layer of graphene covers a fraction, \( \gamma \), of the pores in the PCTEM support, with subsequent layers covering the same fraction of pores independent of the other layers (Fig. 4-1). As a result, a two-layer graphene membrane has polycarbonate pores with zero, one, or two layers of graphene (Fig. 4-1c). The fraction of polycarbonate pores with \( n \) layers of graphene coverage is denoted \( \gamma_n \).

When multiple layers of graphene are stacked, it is assumed that intrinsic defects in one layer are covered by graphene in another layer, except where intrinsic defects in all layers randomly align. The density of through holes created by aligned intrinsic defects is characterized by their average spacing in \( n \) stacked layers of graphene, \( L_{ip}^{(n)} \).

Gas transport through the graphene membrane was computed using an equivalent resistance network\(^8\) (Fig. 4-2). Each branch of this network represents polycarbonate pores with a certain number of layers of graphene coverage, \( i \), and a certain number of intrinsic defects, \( k \). Through pores without graphene, only the support polycarbonate membrane provides resistance to gas flow. Through support pores with graphene suspended over them, defects and intentionally created selective pores act as parallel flow paths through the graphene, with the support membrane resistance acting in series behind the graphene.

The graphene membrane permeance for arbitrary gas \( A \) is then computed as,

\[
P_A = \gamma_0 P_{pC}^A + \sum_{n=1}^{N} \sum_{k=0}^{\infty} \gamma_n f_{n,k} \left[ \frac{1}{P_{pC}^A} + \frac{4k}{\pi} P_{ip,n}^A \left( \frac{L_{ip}^{(n)}}{D_{pC}} \right)^2 + P_S^A \right]^{-1} \tag{4-1}
\]

where \( P_A [\text{mol/m}^2\cdot\text{s-Pa}] \) is the overall membrane permeance to arbitrary gas \( A \) based on total membrane pore area, \( P_{pC}^A [\text{mol/m}^2\cdot\text{s-Pa}] \) is the membrane permeance of the polycarbonate support to gas \( A \) based on total membrane pore area, \( P_S^A [\text{mol/m}^2\cdot\text{s-Pa}] \) is the permeance of the graphene to gas \( A \) due to intentionally created selective pores based on graphene area, \( P_{ip,n}^A [\text{mol/m}^2\cdot\text{s-Pa}] \)
Figure 4-2. Graphene permeance model. a, Illustration of support membrane pores with different numbers of layers of graphene and different numbers of aligned defects. b, Equivalent resistance network for flow through graphene membranes. Note that $R_{PC} = 4(\pi D_{PC}^2 P_{PC}^A)^{-1}$ is the resistance of the support polycarbonate pore, $R_{S} = 4(\pi D_{PC}^2 P_{S}^A)^{-1}$ is the resistance of single selective nanopores in multi-layer graphene, and $R_{ip}^{(n)} = \left(\frac{(n_{ip})^2 P_{ip,n}^A}{f_{ip,n}}\right)^{-1}$ is the resistance of the area of graphene over a single support pore due to intrinsic defects in graphene.

is the average permeance to gas A due to intrinsic defects based on graphene area, $D_{PC}$ [m] is the polycarbonate support membrane pore diameter, and $f_{n,k}$ is the fraction of polycarbonate pores with $n$ layers of graphene coverage that have $k$ intrinsic defects. Here, the summation on $k$ is allowed to go to infinity, even though there is a limit to the number of finite sized defects in graphene over a support pore, because the low probability, $f_{n,k}$, of large $k$ produces negligible contribution to the sum.
4.1.1 Average intrinsic defect spacing

Monte Carlo simulations were used to estimate the average spacing between through holes in multi-layer graphene with this distribution of defect sizes, as a function of intrinsic porosity. This calculation is described in here.

*Average distance between intrinsic defects in one layer of graphene*

In Ref. 35, STEM images were used to determine the distribution of intrinsic defect sizes in one layer of graphene from the same source used in Ch. 3. The size distribution is shown in Fig. 4-3. Here, the “effective diameter” of an intrinsic defect is the diameter of the circle with the same area as the measured intrinsic defect. From this size distribution, the average area of an intrinsic defect is computed as,

\[
\bar{A}_{\text{IP}} = \frac{1}{N_{\text{defects}}} \sum_{i_{\text{IP}}=1}^{N_{\text{defects}}} \pi r_{\text{IP},i_{\text{IP}}}^2
\]

where \( N_{\text{defects}} \) is the number of intrinsic defects imaged in Ref. 35 and \( r_{\text{IP},i_{\text{IP}}} \) is the effective radius of intrinsic defect with index \( i_{\text{IP}} \). The input intrinsic porosity, \( \eta \), which is the area fraction of a single layer of graphene occupied by intrinsic defects, is used to compute the average distance between intrinsic defects in one layer of graphene.

*Figure 4-3. Effective diameter distribution of intrinsic defects measured from STEM images in Ref. 35.*
For an input value of \( \eta \), the Monte Carlo simulation code calculates \( L_{ip}^{(1)} \), then, at each iteration, generates a possible arrangement of defects in five layers of graphene over an area of size \( L_{ip}^{(1)} \times L_{ip}^{(1)} \).

**Placing intrinsic defects**

The number of intrinsic defects in the simulated area, in each layer, is sampled from a Poisson distribution,

\[
P_k = \frac{e^{-1}}{k!}
\]

where \( P_k \) is the probability of \( k \) defects in one layer of graphene over an \( L_{ip}^{(1)} \times L_{ip}^{(1)} \) area. Here, the average number of defects per layer in the area has been set to one by definition. Five values are sampled from this distribution, representing the number of defects in each of the five layers of graphene over this area. For each layer, and for each intrinsic defect in the layer, \( x \) and \( y \) coordinates are randomly sampled uniformly within the area \( L_{ip}^{(1)} \times L_{ip}^{(1)} \) (Fig. 4-4).
A random integer is selected uniformly between 1 and $N_{\text{defects}}$. The radius, $r$, of the intrinsic defect with that index from Fig. 4-3 is assigned to the generated defect. Periodic images of the defects are also placed.

After each intrinsic defect location and radius set is selected, the program checks whether this intrinsic defect, or its periodic images, overlap with any other intrinsic defects, or their periodic images, within the same graphene layer. Since the measured intrinsic defect diameter distribution in Fig. 4-3 already accounts for overlapping defects within the same layer, no two defects are permitted to overlap within the same layer. When sampled defects do overlap, the $x$ and $y$ coordinates of the most recently generated defect are re-sampled. If the program re-samples a defect's coordinates more than $10^5$ times, and all of these samples result in overlapping defects, then it is assumed that no $L_{ip}^{(1)} \times L_{ip}^{(1)}$ area with the previously sampled ($x$, $y$, $r$) sets and a defect with the most recently sampled $r$ value can occur. This $L_{ip}^{(1)} \times L_{ip}^{(1)}$ area is then repeated by discarding previously sampled defects and resampling.

Finding through holes

Once locations and radii are selected for every defect in all five layers, the program counts overlapping defects between layers by checking every combination of intrinsic defects in different layers.

Average distance between intrinsic defects in multi-layer graphene

The program computes the average number of intrinsic defects per $L_{ip}^{(1)} \times L_{ip}^{(1)}$ area in each number of layers of graphene coverage by:

$$\left(\frac{L_{ip}^{(1)}}{L_{ip}^{(6)}}\right)^2 = \frac{\text{total number of through holes counted for } n \text{ layers of graphene coverage}}{\text{number of } L_{ip}^{(1)} \times L_{ip}^{(1)} \text{ areas simulated}}$$

(4-5)
From the above expression, \( L_{IP}^{(n)} \) is computed for each number of layers of graphene, \( n \), and the resulting values are plotted in Fig. 4-5, as the "many small area simulation" results.

**Aligned defect density scaling**

The number density and distance between intrinsic defects is an important parameter governing the membrane performance. Power-law fits to the Monte Carlo simulation results for a range of intrinsic porosities (Fig. 4-5) show a scaling \( (L_{IP}^{(n)})^{-2} \sim \eta^n \), i.e., the average number density of aligned intrinsic defects in independently stacked layers of graphene decreases as the \( n^{th} \) power of the intrinsic porosity of graphene. This scaling behavior is explained by the fact that when a layer of graphene with porosity \( \eta \) is placed on a previous layer, only a fraction \( \eta \) of the existing defects align with defects in the new layer. Therefore, each successive layer reduces the number of defects by a fraction \( \eta \). The exact coefficients of the scaling relations depend on the

![Figure 4-5](image-url)

**Figure 4-5.** Computed average spacing between intrinsic through holes in multi-layer graphene. The plot compares the predicted average distance between intrinsic defects from the "one large area simulation" and the "many small area simulation." A power-law fit to the coefficient, \( a \), in the \( L_{IP}^{(n)} \sim a \eta^{-n/2} \) fit is shown in the inset.
intrinsic defect size distribution. The power-law fits are also used to interpolate values of $L_{ip}^{(n)}$ for values of $\eta$ that were not simulated.

### 4.1.2 Resistance model weighting factors

The computed $L_{ip}^{(n)}$ values are used to calculate terms in the resistance network of Fig. 4-2b. The number of through holes in multi-layer graphene over a polycarbonate pore is assumed to be Poisson distributed. Since the average number of through holes in $n$ layers of graphene over a polycarbonate pore is, $\frac{\pi}{4}(D_{PC}/L_{ip}^{(n)})^2$, the fraction of polycarbonate pores with $n$ layers of graphene coverage that have $k$ intrinsic defects is,

$$f_{n,k} = \frac{1}{k!} \left[ \frac{\pi}{4} \left( \frac{D_{PC}}{L_{ip}^{(n)}} \right)^2 \right]^k \exp \left[ -\frac{\pi}{4} \left( \frac{D_{PC}}{L_{ip}^{(n)}} \right)^2 \right]$$

(4-6)

Assuming that each of the $N$ layers of graphene cover the same fraction, $\gamma$, of polycarbonate pores randomly, and independent of the other layers, the fraction of polycarbonate pores that have $n$ layers of graphene coverage is,

$$\gamma_n = \frac{N!}{n!(N-n)!} (1-\gamma)^{N-n}\gamma^n$$

(4-7)

### 4.1.3 Intrinsic defect permeance

To limit complexity, it was assumed that all intrinsic defects have identical permeance regardless of the size, an approximation that was validated separately (see Section 4.3). Gas molecules were further approximated as point particles. The average permeance due to intrinsic defects in $n$-layer graphene ($P_{ip,n}^A$) was estimated as the equilibrium ideal gas flux through the fraction of graphene area occupied by aligned intrinsic defects, assuming that the intrinsic pores
are much larger than the gas molecules. For \( n \) layer graphene coverage, the average permeance of intrinsic defects is,

\[
P_{p,n} = \frac{\pi D_{PC}^2}{4} \frac{\eta^n}{\sqrt{2\pi M_A R T}}
\]

(4-8)

where \( M_A \) is the molecular weight of the gas.

### 4.1.4 Selective nanopore permeance

Finally, any selective nanopores intentionally introduced into the graphene will provide a flow path in parallel to the intrinsic defects. It was assumed that their density is sufficiently high to represent flow through these nanopores by an average selective pore permeance, \( P_S^A \), defined as the molar flow rate per unit graphene area per unit pressure difference.

Although included in the model, in the experiments in Ch. 3, intentionally created selective nanopores were not generated. Thus, the selective pore permeance is set to zero in analyzing those results, and is revisited in Ch. 5.

### 4.2 Model agreement with measurements

In this section, the accuracy of the model is evaluated by comparison with experimental measurements of gas transport through the multi-layer membranes from Ch. 3. These measurements were for gases covering a wide range of molecule sizes (He, N\(_2\), and SF\(_6\), with kinetic diameters of 2.6 Å, 3.64 Å, and 5.5 Å, respectively\(^{90}\)), without any intentionally created selective nanopores (\( P_S^A = 0 \)).

For comparison to graphene membrane permeance measurements, the polycarbonate support membrane permeance (\( P_{PC}^A \)) for each gas was taken as the measured value on a bare PCTEM without any graphene (Fig. 3-2d,e). This leaves two unspecified parameters in Eq. 4-1:
Figure 4-6. Multi-layer graphene membrane flow rate measurements and model fit. a, Flow rate model fit, giving a coverage of 69.8% (\(\gamma = 0.698\)) and an intrinsic porosity of 0.687% (\(\eta = 0.00687\)). Flow rates are normalized by the value for a bare PCTEM. b, Measured flow rate ratios compared to model fit for flow rates.

(1) the fraction of polycarbonate pores covered by a single layer of graphene, \(\gamma\), and (2) the fraction of graphene area occupied by intrinsic defects, \(\eta\). These values were determined by performing a numerical least-squares fit of Eq. 4-1 with \(P_5^A = 0\), to the experimental data in Fig. 3-5a. The optimal fit was obtained for \(\gamma = 0.698\) and \(\eta = 6.87 \times 10^{-3}\). This inherent permeance (\(\eta\)) corresponds to, on average, 6.5 nm defects with 70 nm spacing (Fig. 4-3, 4-5) and quantifies the typical quality of CVD graphene. The resulting fit is compared to the measurements in Fig. 4-6.

The model results accurately matched the exponential decrease of measured flow rates as the number of layers of graphene was increased (Fig. 4-6a). The model also captures the gradual rise in flow rate ratios of the gases with increasing number of graphene layers. Since the intrinsic defects were measured to be larger than the kinetic diameter of the gases, the intrinsic defect selectivity is approximately \(P_{i,p,1}^A/P_{i,p,1}^B = \sqrt{M_B/M_A}\) from the kinetic theory of gases, which is somewhat higher than that for flow through the polycarbonate pores (Fig. 3-2e). As a result,
increasing the contribution of intrinsic defects compared to tears upon adding more layers of graphene causes a slight increase in the flow rate ratio.

Quantitative agreement between the experimental and theoretical flow rate and flow rate ratio with increasing number of graphene layers provides validation for the model developed here.

### 4.3 Further model validation

The model described above was further verified by comparing its predictions to those of a more detailed model, discussed in this section. This model will be referred to as the “one large area simulation” model, distinguishing it from the “many small area simulation” model described above. It was developed to describe the flow through graphene membranes more accurately by including more details than the “many small area simulation” model. Specifically, this model accounts for the size distribution of intrinsic through holes in the graphene over a polycarbonate pore and the effect of non-zero gas molecule size on the flow rate through intrinsic defects.

In this model, each polycarbonate pore is treated as a separate branch in the equivalent flow rate resistance network, as seen in Fig. 4-7. It is assumed that there are a large number of polycarbonate pores in the membrane, such that all of the pores with a given number of layers of graphene suspended over them can be represented by a single branch in the resistance network. The resistances are computed by sampling a large number of polycarbonate pores. In this network, $R_{PC}$ is the resistance of one support polycarbonate pore, defined as the pressure difference (Pa) applied across it divided by the molar flow rate (mol/s) through it. The graphene resistance consists of the resistance to flow through intrinsic defects in the graphene, $R_{IP_{(l)PC}}^{(n)}$, and the resistance to flow through intentionally created selective nanopores in the graphene, $R_{S_{(l)PC}}$. Both resistances are defined as the pressure difference (Pa) across the graphene over the simulated polycarbonate pore.
with index \( i_{PC} \), divided by the molar flow (mol/s) rate through the graphene, due to either intrinsic
defects (\( R_{IP,i_{PC}}^{(n)} \)) or selective pores (\( R_{S,i_{PC}} \)). The superscript \( n \) indicates the number of layers of
graphene over pore \( i_{PC} \) used to calculate \( R_{IP,i_{PC}}^{(n)} \), since the same simulated support pores are reused
in the calculations with different numbers of layers of graphene. \( R_{IP,i_{PC}}^{(n)} \) and \( R_{S,i_{PC}} \) are determined
separately for each polycarbonate pore and are then combined.

**Polycarbonate pore array**

The resistance to flow through intrinsic defects was calculated using Monte Carlo simulations. Separate simulations were performed for each number of layers of graphene coverage.

In each simulation, a regular array of polycarbonate pores was simulated, as sketched in Fig. 4-8. The smallest distance between polycarbonate pores in the array was set to the largest diameter of any measured intrinsic defect, \( 2r_{IP}^{\text{max}} \). This ensures that an intrinsic defect cannot overlap with two

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**Figure 4-7.** Equivalent resistance network for the “one large area simulation” model.
or more polycarbonate pores. Areas of \((L + 2r_{\text{ip}}^{\text{max}}) \times (L + 2r_{\text{ip}}^{\text{max}})\) at a time were simulated, where \(L\) is the length of the square simulation box where polycarbonate pores can be placed. In this area, arrays of polycarbonate pores of radius \(r_{\text{pc}} = 500\) nm were placed, matching the pore size used in the experiments. In total over \(10^6\) polycarbonate pores were simulated for each intrinsic porosity of graphene \((\eta)\) considered, to provide reliable averages.

After setting up the polycarbonate pore array, the Monte Carlo simulation code then places intrinsic defects in each layer of graphene over the array of polycarbonate pores.

**Placing intrinsic defects**

As done in the "many small areas simulation," the average area of an intrinsic defect, \(\bar{A}_{\text{ip}}\), was computed from the measured size distribution (Fig. 4-3) by Eq. 4-2. Then, for the input area fraction of intrinsic defects in one layer of graphene, \(\eta\), the expected number of intrinsic defects in each layer over the simulated area was estimated as,

\[
N_{\text{defects per layer}} = \text{floor} \left[ \frac{\eta(L + 2r_{\text{ip}}^{\text{max}})^2}{\bar{A}_{\text{ip}}} \right]
\]  

(4-9)

---

**Figure 4-8.** Sketch of a small area of the one large area Monte Carlo simulation setup.
For each layer of graphene, $N_{\text{defects per layer}}$ defects were assigned random $x$ and $y$ coordinates in the $(L + 2r_{\text{ip}}^{\text{max}}) \times (L + 2r_{\text{ip}}^{\text{max}})$ simulation area. The measured defects in Fig. 4-3 were numbered from 1 to $N_{\text{defects}}$. Then, for each simulated intrinsic defect, a random integer between 1 to $N_{\text{defects}}$ was generated and the measured intrinsic defect radius from Fig. 4-3 with that index was assigned to the simulated defect. Before generating the next defect, the program checks whether the defect that was just generated overlaps with any other intrinsic defect in the same layer of graphene. This is not permitted, because the measured intrinsic defect distribution in Fig. 4-3 already includes overlapping defects. The program checks for overlapping intrinsic defects by looping over all previously generated defects within that layer and checking whether,

$$\left( x_{i_n} - x_{j_n} \right)^2 + \left( y_{i_n} - y_{j_n} \right)^2 < \left( r_{i_n} + r_{j_n} \right)^2$$

where $x$, $y$, $r$ are the coordinates and radii of the defect with index $i_n$ or $j_n$, and $n$ indicates which layer of graphene the defect index applies to. If defects are found to overlap within a layer, the $x$ and $y$ coordinates of the most recently generated defect are re-sampled. This process is continued until a defect is generated that does not overlap with any other defects within the same layer.

**Finding through holes and estimating flux**

Once all of the intrinsic defects in each of the graphene layers have been generated, the program finds all areas where intrinsic defects between layers form a through hole. It then computes the fraction, $F$, of incident gas molecules that can pass through these aligned intrinsic defects by a Monte Carlo simulation, considering size exclusion based on the kinetic diameter of the molecule. In this hard sphere throwing simulation, for simplicity, molecules only approach from an angle normal to the graphene plane.
**Intrinsic defect resistance**

Once the fraction of incident gas molecules of helium, nitrogen, and sulfur hexafluoride that pass through intrinsic defects in each polycarbonate pore have been computed, the resistance of the graphene over a polycarbonate pore to gas flow through intrinsic defects can be computed from,

\[
R_{IP,iPC}^{(n)} = \left[ \frac{1}{\sqrt{2\pi M_A RT}} \pi r_{PC}^2 F \right]^{-1}
\]

where \( M_A \) is the molecular weight of the gas.

**Intentionally created selective nanopores**

Using a specified density of intentionally created selective nanopores of \( \rho_S = 10^{12} \) selective-nanopores/cm\(^2\), the number of selective nanopores in the graphene over each polycarbonate pore, \( N_{S,iPC} \), simulated above was assigned by randomly sampling from a Poisson distribution with an average value of \( \rho_S \pi r_{PC}^2 \). The resistance of a single selective nanopore is approximated as constant over all pores, and this value is specified between \( R_S = 10^{19} \) and \( 10^{23} \) selective-nanopores-s-mol/Pa, slightly wider than the expected range based on the measurements of Koenig et al.\(^{33}\) and molecular dynamics simulations by Au.\(^{59}\) This assumes that the intentionally created selective nanopores are straight through all layers of graphene, and that their flow resistance is independent of the number of layers.

**Computing net flow rate resistance**

The resistances of the selective pores are added in parallel to compute an equivalent resistance as,

\[
R_{S,iPC} = \frac{R_S}{N_{S,iPC}}
\]
The resistance of the support membrane to each gas, $R_{PC}$, was determined from measurements of flow rates through bare PCTEMs, shown in Fig. 3-2d,e.

The total resistance through the graphene and polycarbonate pore is then computed as,

$$R_{\text{IPC}}^{(n)} = \left( \frac{1}{R_{S,\text{IPC}}} + \frac{1}{R_{\text{IPC}}^{(n)}} \right)^{-1} + R_{PC}$$ (4-13)

For each number of layers of graphene, an effective resistance was computed such that the network in Fig. 4-7 would only have six branches for a five-layer graphene membrane, corresponding to the collections of polycarbonate pores with zero, one, two, three, four, and five layers of graphene over them.

The equivalent resistance for an ideal graphene membrane with $n$ layers of graphene coverage over every polycarbonate pore is computed by averaging these parallel resistances,

$$R^{(n)} = N_{PC} \left( \sum_{i_{PC}=1}^{N_{PC}} \frac{1}{R_{\text{IPC}}^{(n)}} \right)^{-1}$$ (4-14)

Then, for a specified fraction of polycarbonate pores covered by each layer of graphene, $\gamma$, in an actual $N$ layer composite graphene membrane, the fraction of polycarbonate pores with $n$ layers of graphene over them, $\gamma_n$, can be calculated from Eq. 4-7. These $\gamma_n$ values are used as weighting factors in computing the effective resistance of the overall circuit in Fig. 4-7,

$$R = \left( \sum_{n=0}^{N} \frac{\gamma_n}{R^{(n)}} \right)^{-1}$$ (4-15)

This effective resistance is computed separately for helium, nitrogen, and sulfur hexafluoride. The resistance is defined as the inverse of the product of permeance and pore area, so from these resistances the flow rates and flow rate ratios are obtained.
4.3.1 Model comparison

To verify that the “many small area simulation” model is consistent with the more detailed “one large area simulation” model, intrinsic defect characteristics obtained from both model simulations are compared in Figs. 4-5,4-9,4-10. The “many small area simulation” model assumes that the number of intrinsic defects per polycarbonate pore in multi-layer graphene is Poisson distributed, whereas the “one large area simulation” only assumes that the intrinsic defects in each layer of graphene have a random uniform spatial distribution.

**Figure 4-9.** Comparison of predicted distribution of the number of intrinsic defects per 1 μm diameter polycarbonate pore from “one large area simulation” (green bars) and “many small area simulation” (black curves).
Figure 4-10. Comparison of predicted fraction of incident gas molecules that pass through intrinsic defects in a 1 μm diameter polycarbonate pore with a specified number of layers of graphene (n), intrinsic porosity of graphene (η), and number of intrinsic defects over the polycarbonate pore (k). The average flux from the “one large area simulation” (black, red, and blue markers correspond to helium, nitrogen, and sulfur hexafluoride, respectively) is compared to the “many small area simulation” prediction (black lines).
Figure 4-9 shows histograms of the number of intrinsic defects over a support pore. The black curves show the assumed Poisson distribution from the “many small area simulation” \( (f_{n,k}, \text{Eq. 4-6}) \) based on the computed \( l_{np}^{(n)} \) values. The agreement between these curves and the green bars, which show the resulting distribution of intrinsic defects per polycarbonate pore computed in the “one large area simulation,” validates the assumed intrinsic defect per polycarbonate pore distribution in the “many small area simulation” model.

The “many small area simulation” model also assumes that molecule size is not significant in determining the gas flux through intrinsic defects. This assumption is supported by Fig. 4-10, which shows the fraction of incident gas molecules that pass through intrinsic defects in the graphene over a polycarbonate pore with a specified number of layers of suspended graphene over it and intrinsic porosity of graphene. The markers show the average value of this fraction computed from the “one large area simulation” results for helium, nitrogen, and sulfur hexafluoride. The helium flux is only slightly higher than the nitrogen flux, which is only slightly higher than the sulfur hexafluoride flux. This suggests that the selectivity enhancement of the membrane due to differences in gas molecule sizes restricting flux through intrinsic defects has a negligible effect on the overall membrane selectivity. It should also be noted that data scatter in the markers at relatively high and low numbers of intrinsic defects per polycarbonate pore results from a small sample obtained in the Monte Carlo simulations, as seen in Fig. 4-9.

In the “many small area simulation” model, it is assumed that the permeance of each through hole only depends on the number of layers of graphene and the intrinsic porosity of graphene. Thus, this model assumes that the fraction of incident gas molecules that pass through intrinsic defects in the \( n \) layers of graphene over a polycarbonate pore with \( k \) through holes, \( f_k^{(n)} \), satisfies,
\[
\sum_{k=0}^{\infty} \bar{F}_k^{(n)} f_{n,k} = \eta^n \tag{4-16}
\]

Since every through hole in \( n \) layers of suspended graphene is assumed to have the same permeance in the “many small area simulation” model,

\[
\bar{F}_k^{(n)} = \bar{F}_1^{(n)} k \tag{4-17}
\]

\[
\bar{F}^{(n)} = \frac{\eta^n}{\sum_{k=0}^{\infty} k f_{n,k}} \tag{4-18}
\]

The black line in Fig. 4-10 shows \( \bar{F}_k^{(n)} \) for the computed average distance between intrinsic defects in multi-layer graphene, \( L^{(n)}_{IP} \), from the “many small area simulation.” The close agreement between this line and the markers demonstrates that the finite size of gas molecules also has a negligible effect on the average gas flux through intrinsic defects, further validating the assumptions made in the “many small area simulation” model.

A final comparison is made in Fig. 4-5 between the predicted average distance between through holes computed in the “many small area simulation” and the “one large area simulation”. The values predicted by the “one large area simulation” were computed from the simulation results by applying the following equation separately for polycarbonate pores with each number of layers of graphene \( n \) and intrinsic porosity \( \eta \):

\[
L^{(n)}_{IP} = \sqrt{\frac{\pi r_{PC}^2}{\text{number of polycarbonate pores simulated}}} \left( \frac{\text{number of polycarbonate pores simulated}}{\text{number of through holes}} \right) \tag{4-19}
\]

Due to the greater expense of the “one large area simulation,” it requires relatively long simulation times to obtain accurate \( L^{(n)}_{IP} \) data for large numbers of layers of graphene and low intrinsic porosities. Consequently, in Fig. 4-5, data scatter is apparent as these conditions are approached, with no estimate of \( L^{(n)}_{IP} \) obtained for the extreme cases. The agreement between predicted values
of $L_{ip}^{(n)}$ from the “one large area simulation” and the “many small area simulation” in Fig. 4-5 further verifies the consistency of these two models.

### 4.4 Contribution of interlayer transport

The models developed above attribute the inherent permeance of multi-layer graphene to aligned defects. However, in addition to passing through micrometer-scale tears in multiple layers of graphene and through aligned intrinsic defects, it is possible that gas molecules could cross multi-layer graphene membranes by diffusing between layers. Gas molecules could enter the space between graphene layers through an intrinsic defect in the first layer of graphene that is covered by graphene in the second layer. The gas molecules could then pass through the membrane by diffusing in the space between the layers to an intrinsic defect in the second layer that is covered by graphene in the first layer (Fig. 4-11). This interlayer transport path has been neglected in the previous calculations. In this section, its potential contribution to transport is considered.

#### 4.4.1 Interlayer flux resistance model

It is possible to obtain an upper bound estimate for the gas flux between layers of graphene from the experimental measurements. The data in Fig. 4-6a is replotted on a log-linear scale in

![Figure 4-11. Illustration of possible transport pathways through multi-layer graphene membranes. a, Interlayer transport. b, Transport through aligned defects.](image)

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Fig. 4-12. Comparison of multi-layer graphene permeance measurements to “many small area simulation” model fit. The graph shows the same results as in Fig. 4-6, plotted on a log-linear scale to emphasize the difference between the model and measurements for five-layer graphene.

Fig. 4-12. As seen in this figure, the model predictions match the measured flow rates very well up to four layers of graphene. However, with five layers of graphene, the measured flow rates are appreciably higher than the model predictions.

It is possible that the deviation of the model trends from the measured flow rates for five-layer graphene composite membranes (Fig. 4-12) is due to interlayer gas transport, which scales weakly (inversely) with the number of layers and will eventually govern transport as the number of layers increases. By assuming that this deviation results entirely from interlayer gas transport, the resistance to gas flow between two graphene layers can be computed using the resistance network in Fig. 4-13, which makes the approximation that the interlayer transport resistance is large compared to that through defects in a single layer of graphene. This model also approximates the interlayer gas flux as being independent of the other transport pathways, with the different branches representing areas of two, three, four, and five-layer graphene with only intrinsic defects that are not aligned. The gas flux per unit area across this network is then,
molar flow rate per PCTEM pore = \Delta \phi \frac{m}{R_{II}} \left( y_2 + \frac{1}{2} y_3 + \frac{1}{3} y_4 + \frac{1}{4} y_5 \right) \quad (4-20)

where \Delta \phi \text{ [mol/m}^2] is the difference in two-dimensional concentration (concentration [mol/m}^3] times average effective layer spacing [m]) of gas across the graphene layers; \( m \) is the average number of nanometer-scale intrinsic defects in the area over a single PCTEM pore without micrometer-scale tears; and \( R_{II} \) is the resistance to gas flow in the space between graphene layers, defined as the product of the molar concentration difference (mol/m}^3) across the membrane and the number of defects in one layer, divided by the resulting molar flow rate (mol/s).

The interlayer resistances, and hence, the interlayer permeances were computed from this equation and are presented in Table 4-1. From this result, a conservative lower bound for the interlayer transport resistance for helium is estimated to be \( 1.2 \times 10^4 \text{ Pa-s-m}^2/\text{mol} \). However, such a low interlayer transport resistance would cause significant deviation between measured flow rates and model predictions for two, three, and four layer membranes, which are not observed. For five-layer graphene, the discrepancy is approximately 70% of the total flux. Using the same interlayer resistance (\( R_{II} \)) computed for the five-layer case, the model predicts discrepancies between the modeled and measured gas flow rates in Fig. 4-12 of approximately 5%, 20% and 50% for the two, three, and four layer membranes, respectively, due to neglecting interlayer flux. These errors are significantly larger than those actually observed in Fig. 4-12, indicating that the interlayer resistance is significantly under-predicted. Therefore, it is concluded that interlayer transport is not responsible for the deviation between model and measured flow rates for the five-layer membranes in Fig. 4-12, and the computed interlayer transport resistance represents a very conservative lower bound. The discrepancy between the measurements and model predictions for the five-layer membrane in Fig. 4-12 are thus likely due to damage induced during the repeated
mechanical pressing steps in stacking graphene layers, which could become a significant factor at low flow rates.

A recent report in which transport across stacked graphene layers was measured speculated that the increase in flow rate ratio is due to interlayer transport. The experiments and modeling results presented here indicate that the permeability for interlayer transport in graphene is low and that intrinsic defects alone can account for the increased selectivity observed from stacking successive layers. This result is consistent with measurements of interlayer gas diffusion along a graphene-copper interface, which show significantly lower transport than has been observed between layers of graphene oxide.

4.4.2 Interlayer diffusion model

It is also possible to obtain an upper bound for the gas diffusivity between graphene layers using a diffusion model. It is assumed that the two-dimensional diffusion between graphene layers is the dominant restriction to the gas flow. To simplify the estimate, the intrinsic defects in one layer are modeled as point sources of concentration and the intrinsic defects in the other layer are modeled as concentration sinks (Fig. 4-14a-c). The solution for the concentration field satisfying the two-dimensional scalar Laplace equation is then,

\[
\phi = \sum_{i=1}^{2q} \frac{Q_i}{2\pi} \ln \sqrt{(x - X_i)^2 + (y - Y_i)^2}
\]

(4-21)

where \(\phi\) is the two-dimensional concentration field of gas between graphene layers; \(Q_i\) is the strength of the concentration source located at defect \(i\); \(X_i, Y_i\) are the \(x, y\) coordinates of defect \(i\); and \(q\) is the number of independent intrinsic defects in each layer of graphene in the model.
Placing intrinsic defects

Monte Carlo simulations were performed in which the locations of the sources and sinks, \((X_i, Y_i)\), were selected randomly within a specified square area, such that the surface density of intrinsic defects matched the measured intrinsic defect density (Fig. 4-14c). Intrinsic defects within the same layer were not permitted to overlap since the measured defect size distribution already accounts for this possibility. Defects in different layers were also not permitted to overlap, since the flux due to aligned intrinsic defects was accounted for in the models developed above. Defect locations were re-sampled whenever overlap occurred.

Boundary conditions and numerical solution

In this model, all intrinsic defects were treated as having the average effective radius of measured intrinsic defects. The gas concentration between layers along the circumference of the intrinsic defects was assumed to be approximately constant. The source/sink strengths, \(Q_i\), were thus determined by requiring that the average concentration along the circumference of each defect was the gas concentration on the upstream/downstream side of the graphene (Fig. 4-14a). Periodic

![Figure 4-13. Interlayer transport dominated gas flow rate resistance model.](image)
boundary conditions were applied on the edges of the square domain, and the concentration field was computed including sources/sinks within two domain lengths on either side of the domain. Selecting an upstream concentration of $\Delta \phi$ and a downstream concentration of 0, the source/sink strengths were solved from,

$$CQ = b$$  \hfill (4-22)

where,

![Diagram](image)

Figure 4-14. Interlayer diffusivity estimation. a, Illustration of arrangement of two sources and two sinks in an equal spacing array. The average concentration boundary condition is indicated. b,c, Arrangement of sources and sinks in an equal spacing array (b) and random spacing array (c). d,e, Distribution of computed source/sink flux coefficients for an equal spacing array (d) and random spacing array (e). f, A section of the concentration field computed for an equal spacing array. g, Computed source/sink flux coefficient plotted against minimum spacing to the next source/sink. Black markers are for a randomly spaced array with average defect spacing of $L_{dp}^{(1)}$ computed from the model fit in Section 4.2. Red markers are for equally spaced arrays with different values of the defect spacing. Average flux coefficients, $\bar{c}$, are indicated.
Table 4-1. Interlayer flux upper bound estimate.

| Gas   | Interlayer permeance $(4m/R_{||}^2)$ (mol/m²-s-Pa) | Interlayer diffusivity $\vartheta d$ (m³/s) |
|-------|---------------------------------------------------|------------------------------------------|
| He    | $8.6 \times 10^{-5}$                              | $12 \times 10^{-16}$                     |
| N₂    | $4.0 \times 10^{-5}$                              | $5.6 \times 10^{-16}$                    |
| SF₆   | $3.0 \times 10^{-5}$                              | $4.2 \times 10^{-16}$                    |

Here, $C$ is the matrix of boundary condition coefficients; $X_i^{(0,0)}$ and $Y_i^{(J,K)}$ are the $x$, $y$ coordinates of intrinsic defect $i$, translated to periodic domain $J$ in $x$ and $K$ in $y$; $p$ is the number of periodic images of the domain used in the calculations; $M$ is the number of averaging points used in the numerical implementation of the boundary conditions; $b_i$ is the source/sink boundary concentration value for defect $i$; and $\bar{r}$ is the average defect radius, corresponding to defect area $\bar{A}_{ip}$. From this, the gas flux into point source/sink $i$ was computed as,

$$C_{i_1,i_2} = \frac{1}{2\pi M} \sum_{j=-p}^{p} \sum_{k=-p}^{p} \sum_{m=1}^{M} \ln \left[ X_i^{(0,0)} + \bar{r} \cos \frac{2\pi \rho}{M} - X_i^{(J,K)} \right]^2 + \left[ Y_i^{(0,0)} + \bar{r} \sin \frac{2\pi \rho}{M} - Y_i^{(J,K)} \right]^2$$

(4-23)

$$b_i = \begin{cases} \Delta \phi & \text{for } 1 \leq i \leq q \\ 0 & \text{for } q < i \leq 2q \end{cases}$$

(4-24)

Interlayer flux through intrinsic defect $i = \vartheta d Q_i = c_i \vartheta d \Delta \phi$

(4-25)

where $\vartheta$ is the interlayer gas diffusivity, $d$ is the effective inter-layer spacing, and $c_i$ is the interlayer diffusion flux coefficient for defect $i$ (Fig. 4-14d,e). Averaging over all of the point sources/sinks simulated, the average interlayer flux per intrinsic defect is (Fig. 4-14g),

$$\text{average interlayer flux per defect} = \bar{c} \vartheta d \Delta \phi$$

(4-26)

where $\bar{c}$ is the average interlayer diffusion flux coefficient. From the simulations, $\bar{c} = 1.3$. This also gives an expression for the interlayer resistance in Fig. 4-13 as,

$$R_{||} = \frac{1}{\bar{c} \vartheta d}$$

(4-27)

from which an upper bound for the effective interlayer diffusivity can be computed using the
experimentally estimated $R_{||}$. These values are presented in Table 4-1. The upper bound estimate for the interlayer diffusivity of helium is $\vartheta d = 1.2 \times 10^{-15}$ m$^3$/s.

The solution was also computed for a uniform array of sources and sinks (Fig. 4-14b,d,f,g), giving $\bar{c} = 1.5$ for $L_{ij}^{(1)}$ obtained from the model fit in Section 4.2.

4.5 Conclusions

An equivalent flow rate resistance model was developed to quantitatively explain the inherent permeance of single and multi-layer graphene. The model attributes permeance to the alignment of micrometer-scale tears and nanometer-scale defects in graphene. The support membrane permeance used in the model was obtained from measurements on a PCTEM without graphene. The intrinsic defect permeance was estimated from a defect size distribution measured by high resolution imaging. Graphene fractional area coverage ($\gamma$) and porosity due to intrinsic defects ($\eta$) were used as fitting parameters to match the model to measurements. The fit provides estimates for these measures of graphene quality ($\gamma = 0.698$ and $\eta = 6.87 \times 10^{-3}$). The model accurately captures the measured exponential decay in leakage with number of graphene layers, as well as the gradual rise in flow rate ratio.

The model further provides an explanation for the rise in flow rate ratio. As graphene layers are added, the fraction of leakage flow through intrinsic defects increases compared to that through tears. Tears are micron-scale, with gas flow in a Poiseuille flow regime, governed by viscosity (Fig. 1-1). Intrinsic defects are nanometer-scale, with gas flow in a Knudsen regime, governed by molecular weight. Thus, as the number of layers of graphene increases, the single component gas measurement selectivity increases from near the viscosity ratio towards the root-mass ratio.
The model developed in this chapter provides a quantitative tool to estimate the significance of tears and intrinsic defects in graphene membrane design. Built into this model is the capability to make predictions about overall membrane performance once selective nanopores are introduced. This is the subject of Ch. 5.

The analysis in this chapter further demonstrates that the inherent permeance of multi-layer graphene can be accounted for by the alignment of tears and defects, with negligible contribution coming from interlayer transport. This is in contrast to graphene oxide membranes, where interlayer transport can be significant. From an analysis of the discrepancy between the permeance model and measurements, using an equivalent resistance model developed for interlayer gas transport, bounding estimates of the interlayer permeance (8.6 × 10⁻⁵ mol/m²-s-Pa for He) and in-plane diffusivity (12 × 10⁻₁⁶ m³/s for He) were obtained.
Chapter 5

Defect tolerant membrane design

Non-selective gas leakage through defects in macroscopic areas of graphene are a significant obstacle to the development of practical graphene membranes. Without addressing these defects, leakage flow will likely dominate transport through the membrane, making any contribution through selective nanopores negligible. Requirements on defect sealing, selective pore permeance, and the capability of the support structure to mitigate leakage need to be understood in order to design a membrane that is selectively permeable despite being made from imperfect graphene. This chapter examines how the various aspects of the graphene membrane design contribute to overall performance.

The model developed in Section 4.1 is first applied to predict the performance of graphene membranes measured in Ch. 3 after intentionally created selective pores are introduced. The model is then reduced to a simplified form and studied to develop an understanding of the important membrane design parameters. From this analysis, estimates of optimal membrane design parameters are extracted that should allow selective gas transport despite the presence of defects in the graphene membranes.
5.1 Feasibility of selectivity with defective graphene

The gas transport model developed in Section 4.1 is used in this section to explore whether gas separation may be accomplished in macroscopic, single or few-layer graphene membranes regardless of the presence of defects. The intentionally created selective nanopore permeance is estimated, and used in the model to predict overall membrane selectivities in the presence of intentionally created selective nanopores. In this analysis, two model gases are considered, He and SF\textsubscript{6}.

Based on molecular dynamics simulations\textsuperscript{59} and gas flux measurements by Koenig et al.\textsuperscript{33} (assuming that the reported flux corresponds to one measured pore), the achievable resistance of a single selective nanopore to He is estimated to be in the range of $9 \times 10^{19}$ to $2 \times 10^{22}$ Pa-s/mol. It is assumed that the selective pore density is $10^{12}$ cm\textsuperscript{-2} (one nanopore per $10 \times 10$ nm\textsuperscript{2} area) to calculate the permeance due to selective pores, $P_{S}^{He}$. Based on the measurements of Koenig et al.\textsuperscript{33} the selective pore selectivity is set to $P_{S}^{He}/P_{S}^{SF_{6}} = 15,000$.

It is further assumed that the selective pore permeance of multi-layer graphene is the same as for single-layer graphene. That is, that it is possible to create pores with sufficient size and density in multi-layer graphene that the graphene permeance is the same as that created in single-layer graphene. However, in practice it will likely be more difficult to create a high density of nanopores in multi-layer graphene.

The available graphene quality (specified by $\eta = 6.87 \times 10^{-3}$ and $L_{ip}^{(m)}$ in Fig. 4-5) and the graphene permeance due to selective pores are limited by the graphene synthesis and selective pore creation procedures. However, it is possible to precisely control the support membrane pore size and permeance. Furthermore, through increasing the number of graphene layers on the membrane
or improving the graphene transfer process, it may be possible to enhance the graphene coverage, that is, increase the fraction of support pores without micrometer-scale tears in the graphene over them.

Taking the ratio of permeances (Eq. 4-1) of two arbitrary gas species, A and B, and non-dimensionalizing by the selective pore permeance of species A gives the overall selectivity of the membrane from the model,

\[
\frac{P_A}{P_B} = \frac{\gamma_0 \frac{P_{AC}}{P_{SAC}} + \sum_{n=1}^{N} \sum_{k=0}^{\infty} \gamma_n f_{n,k} \left[ \frac{P_{SA}}{P_{SC}} \left( \frac{4k P_{IP,n}}{\pi} \frac{P_{SA}^A (L_{IP})^2}{D_{PC}} \right) + \frac{P_{SA}^A}{P_{SAC}} \right]^{-1} \right]^{-1}}{\gamma_0 \frac{P_{BC}}{P_{SC}} + \sum_{n=1}^{N} \sum_{k=0}^{\infty} \gamma_n f_{n,k} \left[ \frac{P_{SB}^B}{P_{SA}^B} \left( \frac{4k P_{IP,n}}{\pi} \frac{P_{SB}^B (L_{IP})^2}{D_{PC}} \right) + \frac{P_{SB}^B}{P_{SAC}} \right]^{-1}}
\]

Using the measured resistance to gas flow of the 1 \( \mu \)m diameter PCTEM support pore (Fig. 5-1) and the graphene coverage of \( \sim 70\% \) per layer measured for multi-layer graphene membranes on these support PCTEMs (Ch. 4), Fig. 5-2 presents model predictions of the selectivity, \( P_A/P_B \), for different membrane characteristics. The model predicts that it is unlikely that any selectivity will
be obtained even with five layers of graphene for the expected range of selective pore permeance (Fig. 5-2, top left plot). This lack of selectivity results primarily from the high permeance of polycarbonate pores, causing leakage through micrometer-scale tears to dominate. By increasing the polycarbonate pore resistance to mitigate the effect of leakage through tears, it is possible to achieve modest selectivity with five layers of graphene (Fig. 5-2, top row of plots). Further increase in polycarbonate pore resistance reduces selectivity because flow is then limited by the non-selective polycarbonate pores.

Figure 5-2. Model predictions of helium (He) to sulfur hexafluoride (SF₆) flow rate ratios for various values of graphene fractional area coverage (γ), support membrane pore diameter (D_pc), and support membrane pore resistance (R_pc).
Using polycarbonate membranes with the smallest commercially available pore size of 10 nm shows the potential for much better selectivity (Fig. 5-2, center row of plots), using the experimentally measured resistance of those polycarbonate membranes (Fig. 5-1). Since the support membrane pore diameter is much smaller than the average distance between intrinsic defects (see Fig. 4-5) it tends to isolate the defects to only a small fraction of graphene-covered polycarbonate pores, leaving the majority of the pores covered with defect-free graphene (Fig. 5-3).

Increasing the number of layers of graphene reduces leakage. Furthermore, if the support membrane pore permeance can be tuned, matching its value to that of the selective pores in graphene can mitigate the effects of tears in the graphene (Fig. 5-4). Three layers of graphene and a factor of 1000 increase of the polycarbonate pore resistance further mitigates leakage, yielding selectivities on the order of 100. With a modest increase in the fractional area coverage of graphene

![Figure 5-3](image-url)

*Figure 5-3.* Illustration of defect isolation by reducing the support membrane pore size. a,b. Many defects act in parallel across a large support pore. c,d. Defects are isolated to a small fraction of the support pores by selecting a sufficiently small support pore size.
from 70\% to 85\%, selectivities on the order of 1000 are feasible (Fig. 5-2, bottom row of plots). These results suggest the feasibility of gas separation using graphene with typical quality obtained by chemical vapor deposition (Section 4-2), provided that an appropriate porous support is chosen.

5.2 Simplified single-layer graphene membrane model

While the above model captures the details of the membranes being fabricated in this work, its complexity makes it difficult to gain strong insights into graphene membrane design optimization. For this reason, in this section, a simplified single-layer graphene permeance model is developed.

In this model, instead of performing Monte Carlo simulations to determine the intrinsic defect permeance of graphene over a large sample of polycarbonate pores, all intrinsic defects are approximated as having the same constant permeance. However, the location of defects is still assumed to be random with uniform spatial distribution. This model does not explicitly account for the size of intrinsic defects and assumes that their size is smaller than that of polycarbonate pores, \( i.e., \sqrt{\eta L_{IP}^{(1)}} \leq D_{PC} \), which remains valid for polycarbonate pore sizes greater than

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**Figure 5-4.** Illustration of tear mitigation by support membrane resistance tuning. In a membrane with tears in the graphene over some of the support pores, selective transport may still be possible if the support pore resistance is matched to the selective nanopore resistance.
approximately 10 nm. However, when the polycarbonate pore size is smaller than the size of intrinsic defects, the graphene coverage effectively becomes $\gamma(1 - \eta)$.

For a given average distance between intrinsic defects, $L^{(1)}_{IP}$, the fraction of polycarbonate pores with $k$ intrinsic defects, $f_{1,k}$, can be calculated from a Poisson distribution by Eq. 4-6 with $n = 1$.

**Resistance model**

The equivalent resistance network for such a one layer graphene membrane is sketched in Fig. 5-5. Note that whereas $R_{PC}$ and $R_s$ are on a per polycarbonate pore basis, $R_{IP}^{(n)}$ is on a per intrinsic defect basis. An expression for the equivalent resistance of the circuit in Fig. 5-5 is found by combining resistances as follows,

\[
\frac{R_{PC}}{1 - \gamma} + \frac{R_{IP}^{(1)}}{f_{1,k} \gamma k} + \frac{R_s}{f_{1,k} \gamma} = \frac{R_{PC}}{f_{1,k} \gamma}
\]

**Figure 5-5.** General one layer graphene resistance model.
\[
\frac{1}{R^{(n)}} = \frac{1}{R_{PC}} + \sum_{k=0}^{\infty} \frac{R_{PC}}{\gamma f_{1,k}} + \frac{1}{R_{S}} + \frac{1}{R_{SPC}} + \frac{1}{R_{SPC}} + \frac{1}{R_{S}}
\] (5-2)

Converting resistance to permeance and non-dimensionalizing by the permeance of selective pores to species A gives the net permeance of the composite membrane to arbitrary gas species A and B,

\[
\frac{p_A}{p_S} = (1 - \gamma) \frac{p_{PC}^A}{p_S^A} + \sum_{k=0}^{\infty} \gamma f_{1,k} \left[ \frac{p_{PC}^A}{p_{PC}^A} + \frac{4k p_{IP,1}^A (L_{IP}^{(1)})^2}{\pi p_{PC}^A} + \frac{1}{D_{PC}} + 1 \right]^{-1}
\] (5-3)

\[
\frac{p_B}{p_S} = (1 - \gamma) \frac{p_{PC}^B}{p_S^B} + \sum_{k=0}^{\infty} \gamma f_{1,k} \left[ \frac{p_{PC}^B}{p_{PC}^B} + \frac{4k p_{IP,1}^B (L_{IP}^{(1)})^2}{\pi p_{PC}^B} + \frac{1}{D_{PC}} + 1 \right]^{-1}
\] (5-4)

Taking the ratio of these two expressions gives the membrane selectivity,

\[
\frac{p_A}{p_B} = \frac{(1 - \gamma) \frac{p_{PC}^A}{p_S^A} + \sum_{k=0}^{k_{\infty}} \gamma f_{1,k} \left[ \frac{p_{PC}^A}{p_{PC}^A} + \frac{4k p_{IP,1}^A (L_{IP}^{(1)})^2}{\pi p_{PC}^A} + \frac{1}{D_{PC}} + 1 \right]^{-1}}{(1 - \gamma) \frac{p_{PC}^B}{p_S^B} + \sum_{k=0}^{k_{\infty}} \gamma f_{1,k} \left[ \frac{p_{PC}^B}{p_{PC}^B} + \frac{4k p_{IP,1}^B (L_{IP}^{(1)})^2}{\pi p_{PC}^B} + \frac{1}{D_{PC}} + 1 \right]^{-1}}
\] (5-5)

Numerically, the infinite sums are computed for \( k = 0 \) to \( k_{\infty} \), where \( k_{\infty} \) is defined as the smallest integer for which \( \sum_{k=0}^{k_{\infty}} f_{1,k} > 0.99999 \). From Eq. 5-5, it can be seen that the selectivity ratio has the following dependence,

\[
\frac{p_A}{p_B} = f \left( \gamma, \frac{L_{IP}^{(1)}}{D_{PC}}, \frac{p_{PC}^A}{p_S^A}, \frac{p_{PC}^B}{p_S^B}, \frac{p_{IP,1}^A}{p_{PC}^A}, \frac{p_{IP,1}^B}{p_{PC}^B} \right)
\] (5-6)
This expression can be further simplified by making a few reasonable approximations for permeances.

Permeance approximation simplifications

If it is assumed that the gases are ideal and that intrinsic defects have no selectivity enhancement over the ideal gas flux ratio, and further assumed that the Knudsen number in the support membrane pores is high, then

\[
\frac{P_{iP,1}^B}{P_{iP,1}^A} = \frac{P_{iP,1}^B}{P_{iP,1}^B} = \sqrt{\frac{M_A}{M_B}}
\]  

(5-7)

The average intrinsic defect permeance on a per polycarbonate pore basis for an arbitrary species A is computed from,

\[
P_{iP,1}^A = \left(\frac{L_{iP}^{(1)}}{R_{iP,1}^A}\right)^2 = \frac{\pi D_{PC}^2}{4} \frac{\eta}{\sqrt{2\pi M_A RT}}
\]  

(5-8)

This eliminates two parameters from the functional dependence of the overall membrane selectivity, reducing this dependence to,

\[
\frac{P^A}{P^B} = f\left(\gamma, \frac{L_{iP}^{(1)}}{D_{PC}}, \frac{P_{PC}^A}{P_{SP}^A}, \frac{P_{iP,1}^A}{P_{SP}^A}, \frac{P_{SP}^B}{P_{SP}^A}\right)
\]  

(5-9)

For simplicity of notation, for this reduced model, some superscripts identifying gas A and that there is a single layer are omitted, i.e.,

\[
\frac{P^A}{P^B} = f\left(\gamma, \frac{L_{iP}}{D_{PC}}, \frac{P_{PC}}{P_{SP}^A}, \frac{P_{iP}}{P_{SP}^A}, \frac{P_{SP}^B}{P_{SP}^A}\right)
\]  

(5-10)
5.3 Model insights into graphene membrane operation

Eq. 5-10 specifies the dimensionless parameters defining gas permeation regimes through single-layer graphene membranes, which can guide their design and optimization. The number of intrinsic defects per polycarbonate pore is proportional to \((D_{PC}/L_{IP})^2\). \(P_{PC}/P_{S}^A\) and \(P_{IP}/P_{S}^A\) define the permeance of the support membrane and intrinsic defects, respectively, relative to that due to selective pores, while the selectivity of the selective pores is defined by \(P_{S}^A/P_{S}^B\). Based on the intentionally created selective nanopore hydrogen/nitrogen selectivity measured on a micrometer-scale graphene membrane by Koenig et al., the selective nanopore selectivity is set to \(P_{S}^A/P_{S}^B = 15,000\) for this analysis.

Given a certain intrinsic defect permeance \((P_{IP}/P_{S}^A)\), both the graphene membrane selectivity \((P^A/P^B, \text{Eq. } 5-5)\) and permeance \((P^A/P_S^A, \text{Eq. } 5-3)\) are defined by the choice of support permeance \((P_{PC}/P_S^A)\) and intrinsic defect spacing relative to the support pore size \((L_{IP}/D_{PC})\). This results in a trade-off between the selectivity \((P^A/P^B)\) and permeance \((P^A/P_S^A)\), illustrated for \(P_{IP}/P_S^A = 0.01\) and \(P_{IP}/P_S^A = 1\) for \(\gamma = 0.99\) (Fig. 5-6a,b). When the permeance of intrinsic defects is small (Fig. 5-6a), high graphene membrane selectivity can be achieved for any value of \(L_{IP}/D_{PC}\). However, for \(P_{IP}/P_S^A = 1\) (Fig. 5-6b) high selectivity is only achieved when the spacing between intrinsic defects is large compared to the support pore diameter \((L_{IP}/D_{PC} \geq 1)\). This illustrates that, when the selective pore permeance dominates over the intrinsic defect permeance, intrinsic defects in the graphene over the support membrane pore will not compromise selectivity. However, when the intrinsic defect permeance is significant, it is important that the support membrane pore diameter be sufficiently smaller than the intrinsic defect spacing, so that the intrinsic defects will be isolated to a small fraction of the support pores, leaving a large number of
support pores with high selectivity. In addition to the dependence on $L_{IP}/D_{PC}$, the membrane is selective only for a certain range of permeance $P^A/P^S$. Non-selective transport through tears results in poor selectivity at high $P^A/P^S$, corresponding to high $P_{PC}/P^S$, whereas the dominant non-selective backing membrane resistance prevents selective transport at low $P^A/P^S$, corresponding to low $P_{PC}/P^S$. Selectivity is observed at intermediate $P^A/P^S$ values, when the support resistance approaches the selective pore permeance $P_{PC}/P^S \sim 1$. Further reduction in the support permeance reduces the total permeance by several orders of magnitude for only modest gain in selectivity.

Figure 5-6. Model predictions of the general graphene membrane permeance characteristics. a,b, Dependence of membrane selectivity $(P^A/P^B)$ on membrane permeance $(P^A/P^S)$ and intrinsic defect spacing $(L_{IP}/D_{PC})$ for 99% coverage ($\gamma = 0.99$) and intrinsic defect permeance of (a) $P_{IP}/P^A = 0.01$ and (b) $P_{IP}/P^A = 1$. c,d, Dependence of (c) membrane permeance $(P^A/P^S)$ and (b) membrane selectivity $(P^A/P^B)$ on the intrinsic defect permeance $(P_{IP}/P^A)$ and intrinsic defect spacing $(L_{IP}/D_{PC})$ for 99% coverage ($\gamma = 0.99$) when the support membrane is matched to that of the selective pores ($P_{PC}/P^S = 1$). e, Support membrane permeance $(P_{PC}/P^S)$ that maximizes membrane selectivity $(P^A/P^B)$ for various graphene area coverage fractions ($\gamma$), intrinsic defect permeances $(P_{IP}/P^A)$, and intrinsic defect spacings $(L_{IP}/D_{PC})$, and f, corresponding maximum membrane selectivities $(P^A/P^B)$. 
When the support membrane resistance matches that of the selective pores \((P_{pc}/P^A_s = 1)\), high permeance occurs for large \(P_{lp}/P^A_s\) and small \(L_{lp}/D_{pc}\) (Fig. 5-6c), for which all support pores have highly permeable intrinsic defects in the graphene over them resulting in poor selectivity (Fig. 5-6d, 5-7). Under these conditions, \(P^A/PS^A = P_{pc}/P^A_s = 1\), because the resistance of the graphene becomes negligible compared to that of the support membrane.

For low intrinsic defect permeance \(P_{lp}/PS\) or large spacing between intrinsic defects \(L_{lp}/D_{pc}\), transport through intrinsic defects becomes negligible and the permeance approaches

\[
\frac{P^A}{P^A_s} = (1 - \gamma) \frac{P^A_{pc}}{P^A_s} + \frac{\gamma}{(1 + P^A_s/P^A_{pc})}
\]  

(5-11)

from Eq. 5-3. The corresponding selectivity, from Eq. 5-5, is,

\[
\frac{P^A}{P^B} = \frac{1 - \gamma) \frac{P^A_{pc}}{P^A_s} + \gamma \left( \frac{P^A_s}{P^A_{pc}} + 1 \right)^{-1}}{(1 - \gamma) \frac{P^A_{pc}}{P^A_s} + \gamma \left( \frac{P^A_s}{P^A_{pc}} + \frac{P^A_l}{P^A_{lp}} \right)^{-1}}
\]  

(5-12)

It is immediately seen from Fig. 5-6d that, even for a properly balanced membrane, selective transport is possible only if either of the two criteria are met: (1) the permeance due to intrinsic defects is small compared to the permeance due to selective pores \((P_{lp}/PS^A \ll 1)\), or (2) the spacing between intrinsic defects is large compared to the support pore diameter \((L_{lp}/D_{pc} \gg 1)\). The first criterion implies insignificant leakage through intrinsic defects. This is unlikely for the currently available quality of graphene (Section 4-2), based on the estimated \(\eta\) and permeance due to selective pores, which suggest \(2 \leq P_{lp}/PS^A \leq 2 \times 10^4\). However, if leakage due to intrinsic defects is negligible with advances in graphene quality and selective pore creation, the selectivity is governed by micrometer-scale tears.
For an approximately balanced support membrane with $P_{PC}^A/P_S^A = 1$, in the low intrinsic defect leakage limit, with perfectly selective intentionally created nanopores ($P_S^A/P_S^B \rightarrow \infty$), Eq. 5-11 shows that the overall membrane selectivity approaches

$$\frac{P^A}{P^B} = \frac{1 - \frac{3}{2}y}{1 - y} \quad (5-13)$$

The second criterion results in isolation of intrinsic defects. Under these conditions, most of the support membrane pores have no intrinsic defects in the graphene suspended over them and flow through intrinsic defects can be restricted by controlling the support membrane pore resistance, enabling high overall membrane selectivity. Leakage is then limited to the remaining pores that have graphene with intrinsic defects, approaching the same selectivity limit, $P^A/P^B = (1 - \frac{3}{2}y)/(1 - y)$. The non-selective regime occurs when these two criteria are not satisfied, and it is not possible to achieve selectivity through control of the support membrane resistance. In this regime, the support membrane pore diameter is larger than the average distance between intrinsic defects ($L_{IP}/D_{PC} < 1$), resulting in most of the support membrane pores having intrinsic defects in the graphene over them. Consequently, the gas flow into the support membrane pores is
dominated by the lower resistance path through the intrinsic defects, bypassing the selective
nanopores and producing no detectable overall membrane selectivity.

5.4 Support membrane selection

The question of how to select an appropriate support membrane to achieve gas separation
for graphene of a given quality, as characterized by the distance between intrinsic defects and the
permeance due to intrinsic defects, is now addressed. The support membrane permeance that
maximizes selectivity and the corresponding maximum possible selectivity depend on the quality
of graphene (Fig. 5-6e,f, 5-7). As in Fig. 5-6d, selectivity requires either low $P_{IP}/P_{S}^A$ or high
$L_{IP}/D_{PC}$.

In the limit of low intrinsic defect leakage, the optimal support membrane resistance is
obtained by solving,

$$\frac{\partial(P^A/P^B)}{\partial(P_{PC}^A/P_{S}^A)} = 0$$

for $P_{PC}^A/P_{S}^A$ from Eq. 5-12. This gives,

$$\left(\frac{P_{PC}^A}{P_{S}^A}\right)_{@\text{max}} = \frac{P_{S}^B}{P_{S}^A} \frac{1}{1 - \gamma}$$

(5-15)

Substituting into Eq. 5-11 gives the maximum selectivity as,

$$\left(\frac{P^A}{P^B}\right)_{\text{max}} = \left(\frac{P_{S}^B}{P_{S}^A} \frac{1 - \gamma + 1}{\sqrt{P_{S}^A + \sqrt{1 - \gamma}}}\right)^2$$

(5-16)

Furthermore, in the ideal case, in which intentionally created selective nanopores are perfectly
selective ($P_{S}^A/P_{S}^B \rightarrow \infty$), the maximum selectivity approaches,
\[
\left( \frac{P^A}{P^B} \right)_{\text{max}} = \frac{1}{1 - \gamma}
\] (5-17)

This differs from the result for the approximately balanced support membrane with \( P_{pc}/P_S^A = 1 \) (Eq. 5-13) for which \( P^A/P^B = \left( 1 - \frac{1}{2} \gamma \right)/(1 - \gamma) \). However, as seen by comparing the plot in Fig. 5-6f to Fig. 5-6d for \( \gamma = 0.99 \), selectivity is not significantly compromised with a membrane permeance of \( P_{pc}/P_S^A = 1 \) instead of the optimal value of \( P_{pc}/P_S^A = 0.082 \), due to the relatively wide peak observed for high \( L_{1p}/D_{pc} \) in Fig. 5-6a,b. However, choosing a support permeance of \( P_{pc}/P_S^A = 0.082 \) drastically compromises the overall membrane permeance, which shows that approximately matching the support permeance to that of selective pores \((P_{pc}/P_S^A \sim 1)\) is practical, rather than optimizing the support permeance for selectivity.

These results demonstrate that by choosing a support membrane with appropriate resistance and with a smaller pore size than the average distance between intrinsic defects, it is possible to achieve selective gas transport despite the presence of defects. While the design of a porous support with isolated cylindrical pores has been discussed, the results can also inform the design of membranes where the support comprises a thin isotropic layer with controlled permeance. In this case, the thickness of the layer is the characteristic dimension that replaces the support pore diameter \( D_{pc} \) in the above analysis, \textit{i.e.}, it is important to choose a thickness that is smaller than the spacing between intrinsic defects. The results in Fig. 5-6 can then be used to identify the appropriate support membrane pore size (or thickness) and permeance once the graphene coverage, intrinsic defect characteristics, and achievable selective pore performance have been estimated.
5.5 Defect tolerant membrane development

The insights gained from modeling gas transport through graphene membranes identify aspects of the membrane design that should be focused on. Specifically, the model quantifies the effects tear and defect density reduction, support structure tuning by resistance matching and defect isolation, and generated selective nanopore permeance on overall membrane permeance and selectivity. With the desired membrane structure in mind, and quantitative predictions of the required design parameters to achieve selective transport, the remainder of this work focuses on the fabrication of defect tolerant graphene membranes.

---

Figure 5-8. Chart of membrane design control parameters (central column) and methods to tune them (right column).
Figure 5-8 summarizes the methods that have been explored to control the various aspects of membrane design. The following chapters detail this work. Chapter 6 discusses methods to reduce the density of tears and defects in graphene. This is done by improving the initial graphene quality, and then sealing remaining holes using additional graphene layers or plugging them with other materials (atomic layer deposition and interfacial polymerization).

Chapter 7 covers support membrane optimization. Two general classes of support membranes show promise: (1) small diameter pore supports and (2) thin dense supports. With small diameter supports, defect isolation is accomplished by choosing a pore size smaller than the average defect spacing. The pore structure is chosen to provide a support permeance in the desired range. With thin dense supports, defect isolation can be accomplished by choosing a layer thickness that is smaller than the average defect spacing, preventing spreading of leakage flow in the material and interaction between defects. Choice of layer thickness and material controls the support permeance.

Chapter 8 describes the selective nanopore generation process and resulting membrane performance. Various selective nanopore generation methods are explored. Ion bombardment at high density is used to perforate the graphene layers. Alternatively, low density ion bombardment is used to nucleate defects in graphene, which are then enlarged into selective nanopores by etching. For this purpose, acidic potassium permanganate etching, UV-ozone etching, and oxygen plasma etching are each considered.

5.6 Conclusions

Using the permeance model developed in Section 4.1 and selective nanopore permeance estimated from published experimental measurements on gas transport through single graphene
nanopores as well as molecular dynamics simulations, it was shown that selective gas transport through macroscopic graphene membranes should be possible despite the presence of defects in graphene. From this, and a simplified model for gas transport in single-layer graphene, the important design features of a selective graphene membrane were identified. Most significantly, design parameters of an optimized support membrane structure were identified, which will mitigate leakage through tears and defects. Methods were outlined to reduce the defect density in macroscopic areas of graphene, to fabricate a membrane with the desired support properties, and to generate selective nanopores. These methods are investigated in the following chapters.
Chapter 6

Defect density reduction

From the graphene inherent permeance measurements and modeling in Ch. 3-5, it is clear that the micron-scale tears and nanometer-scale defects present in macroscopic graphene membranes can compromise membrane performance. Without addressing these defects, it is unlikely that a membrane will be selectively permeable to gases even after selective nanopores are created. This and the next chapter discuss membrane structure and fabrication methods explored to deal with these imperfections. This chapter covers methods to reduce or seal tears and intrinsic defects. Chapter 7 describes methods to mitigate the effects of remaining leakage flow by support membrane structure design.

6.1 Graphene quality

One way to reduce the leakage through defects is to reduce their density in a single layer of graphene (Fig. 6-1). Synthesizing or choosing graphene with a lower intrinsic defect density can reduce leakage. The graphene source also affects the tear density. More hydrophobic graphene on copper tends to prevent wicking of ammonium persulfate between the graphene and support
membrane during graphene transfer. This prevents etching of copper from the graphene side, which damages the graphene. Choosing a more strongly hydrophobic support membrane also discourages ammonium persulfate wicking between the support and the graphene, and can similarly improve the quality of graphene following transfer.

Furthermore, ensuring that the underlying copper is not oxidized before or during graphene growth prevents millimeter-scale gaps in graphene coverage on the copper that are visible after transfer (Fig. 6-2a,b). Note that this is different from observations of increased hydrophobicity of graphene with aging due to exposure to the atmosphere, which can cause a build-up of contamination on the surface and oxidation of the underlying copper.\textsuperscript{93} Such effects could potentially improve the graphene transfer quality. This oxidation occurs following graphene

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6-1.png}
\caption{Map of flow rate ratio and reduction in helium flow rate, compared to a bare PCTEM, for various graphene sources. Graphene was transferred to 200 nm pore PCTEM. Contours show model predictions for various graphene qualities. Commercial graphene sources: Graphene Supermarket, Graphenea, ACS Materials from 2012 and 2014. Graphene prepared by Karnik lab (in lab) is synthesized on nitric acid cleaned copper foil (JX Holdings, electrodeposited or cold rolled) by low pressure chemical vapor deposition at 1050°C.\textsuperscript{94,95}}
\end{figure}
growth on copper, leaving the graphene intact. However, if areas on the copper foil are heavily oxidized prior to graphene synthesis, this could interfere with graphene growth, leaving gaps in the graphene coverage on the copper foil that will remain after transfer to the support membrane.

Figure 6-1 illustrates a simple method to compare the quality of graphene from different sources for membrane applications. Graphene from various sources was transferred onto 200 nm PCTEM supports. Helium and sulfur hexafluoride flow rates were measured through the membranes. The resulting selectivity is plotted against the reduction in helium flow rate compared to the PCTEM without graphene.

Assuming the intrinsic defect distribution imaged on ACS Materials graphene (Fig. 4-3), predictions of the graphene permeance model from Section 4.1 are plotted as contours for comparison. They show how the selectivity-permeance map can be used to estimate porosity due to intrinsic defects ($\eta$) and due to tears (1-$\gamma$). For low graphene coverage, reducing the tear density (increasing $\gamma$) results in reduced He and SF$_6$ flow through the membrane. In this region, for a given

Figure 6-2. Graphene quality inconsistency. a, Poor quality graphene from ACS Materials in 2014. Photographs of approximately 7 mm pieces of graphene on copper show significant areas of oxidized copper. b, The resulting transfers of ACS Materials graphene from 2014 to 200 nm pore PCTEMs show visible gaps in graphene coverage. c,d, This is in contrast to the high quality transfers of ACS Materials graphene from 2012 (c, three-layer) and Graphenea graphene from 2015 (d, single-layer).
graphene coverage ($\gamma$), graphene with higher intrinsic defect density ($\eta$) shows slightly higher selectivity because there are more defects, with near Knudsen selectivity, contributing to the permeance. However, as coverage increases, the helium leakage through membranes with high intrinsic defect density remains high, because even with 100% graphene coverage, there is still significant permeance through intrinsic defects. In this regime, reduced helium flow rates are more related to lower intrinsic porosity, whereas higher selectivities result more from higher coverages.

Membranes with lower intrinsic defect density continue to show reduced leakage as coverage increases. Eventually, with high coverage, these membranes show higher selectivity than the bare PCTEM as transport becomes dominated by that through the intrinsic defects. With 100% coverage, the selectivity is still dependent on the intrinsic defect density. Higher intrinsic defect density means that the resistance to flow of the graphene is lower, closer to that of the PCTEM. Consequently, the lower selectivity of the PCTEM behind the graphene compared to the intrinsic defects averages to a lower selectivity for higher intrinsic defect porosity.

At lower graphene coverages (constant $\gamma$), the selectivity-permeance contours are curved. At high coverages, selectivity increases with decreasing intrinsic defect density and then decreases. As intrinsic porosity decreases, the resistance to flow through defects increases compared to the PCTEM, resulting in a greater contribution of intrinsic defects to the selectivity. This causes selectivity to increase. However, for any graphene coverage less than 100%, leakage through tears will dominate at very low intrinsic porosity. Consequently, as intrinsic defect porosity decreases further, selectivity decreases towards that of the support pores.

The graphene quality contours ($\gamma, \eta$) plotted in Fig. 6-1 were computed assuming the measured intrinsic defect distribution in Fig. 4-3. However, the contours are relatively insensitive to the specific defect size distribution assumed, provided that the defects are sufficiently large that
they do not act as molecular sieves. This is because the plotted contours are specifically for graphene over 200 nm PCTEM pores, which have significantly lower resistance than the intrinsic defects. However, if these contours were computed for significantly smaller PCTEM pores, lower intrinsic porosity, or a better matched support resistance, the defect size distribution would be important in the calculations.

6.1.1 Graphene selection

Mapping measured graphene selectivity-permeance in this way can be used to compare the quality of graphene from different sources and monitor consistency between batches of graphene. For example, in Fig. 6-1, Graphenea graphene shows lower intrinsic defect density whereas graphene prepared by Karnik lab on JX holdings electrodeposited copper shows higher coverage. Thus, Graphenea graphene may be more suitable if fabrication methods are available that can more effectively seal micron-scale tears in the graphene, whereas graphene synthesized on electrodeposited copper may be the better choice if methods of sealing nanometer-scale intrinsic defects are more effective.

Figure 6-1 also illustrates how consistency can be an issue with using commercial sources of graphene. This plot shows measurements of graphene transfers performed with ACS Materials graphene in 2012 and 2014, using graphene from those years. In 2012, ACS Materials graphene on 200 nm PCTEMs had very low tear and intrinsic defect density. However, in 2014, the material quality was significantly lower. Figure 6-2a,b shows what is believed to be the issue with this new material. It appears that some areas of the copper are oxidized. After transfer, there are millimeter-scale gaps in the graphene coverage, similar in size and spacing to the observed oxidized regions on the original copper. This suggests that there were gaps in the graphene before transfer.
These transfers are compared to a transfer of ACS Materials graphene from 2012 (Fig. 6-2c) showing no large gaps in coverage. A Graphenea graphene transfer is similar in appearance (Fig. 6-2d) and was also measured to have relatively low tear and intrinsic defect density.

As a result of the variability in graphene quality, the graphene source for experiments has changed over the course of this work. Initially, experiments were conducted on ACS Materials graphene. In later experiments, Graphenea graphene and graphene prepared by Karnik lab have been used. A major advantage of synthesizing graphene instead of using a commercial source is control over production, which can help reduce batch to batch variability or significant changes in quality.

6.1.2 Graphene synthesis methods

The graphene synthesized by Karnik lab, which is compared to others in Fig. 6-1, was prepared by low pressure chemical vapor deposition. \(^{94,95}\) Copper foil was dipped in 10% nitric acid to remove the oxide layer. It was then placed in a quartz crystal tube furnace in a 4 Torr hydrogen atmosphere (100 SCCM) and heated to 1050°C for 1 h. This melts the copper surface to increase grain size. Methane and hydrogen are flowed at 3.5 and 60 SCCM, respectively. After 30 min, the methane flow rate is increased to 7 SCCM. This step is intended to adsorb additional carbon on copper exposed by defects in graphene to form graphene patches over defects. The tube is then cooled to room temperature by natural convection.

6.2 Multi-layer graphene

As seen in Fig. 6-1, regardless of the choice of graphene source, macroscopic areas of graphene have defects. Chapters 3 and 4 have explored the use of multi-layer graphene to seal tears
Figure 6-3. Illustration of defect sealing. a, Unsealed membrane consisting of graphene over a PCTEM with tears and intrinsic defect. b, Nanometer-scale defects can be sealed by ALD (red). c, Micron-scale tears can be sealed by interfacial polymerization (green).

and intrinsic defects in graphene. It was shown that this approach can exponentially reduce leakage through the membrane. This is a viable method of defect sealing, and is used in a membrane design discussed in Ch. 8.

A potential challenge in using multi-layer graphene membranes is that selective nanopore generation may be more difficult than for single-layer membranes. Ion bombardment may not nucleate defects in all layers. Etching methods may not open up pores in all layers or may create very large non-selective pores in single-layer areas of the membrane before multi-layer regions become porous, reducing the overall graphene permeance through selective pores. For this reason, defect sealing methods for single-layer membranes are desirable.
6.3 Intrinsic defect sealing

Atomic layer deposition (ALD) on a suspended graphene substrate has been shown to preferentially deposit material on defect sites in graphene, and not to nucleate on the pristine lattice. This property could potentially be exploited to seal nanometer-scale intrinsic defects in graphene by depositing enough of an impermeable material to cover defect sites (Fig. 6-3b).

ALD is a process that can controllably deposit monolayers of material. The substrate is exposed to a gas phase precursor that adsorbs on the surface. It is then exposed to a second gas phase precursor that reacts with the adsorbed molecules to leave a layer of bonded material (Fig. 6-4). This process is repeated to build up layers of material. When the substrate is graphene, precursors tend to absorb on higher energy defect sites, resulting in material deposition there. In order for this approach to be successful, it is necessary that ALD growth over the defect be sufficiently fast compared to lateral growth of ALD along the graphene away from defect sites that graphene area remains exposed following ALD.

6.3.1 ALD methodology

Prior to placing membranes (200 or 10 nm support pore PCTEMs with or without graphene) in the ALD chamber (Cambridge NanoTech, Savannah ALD system at the Harvard Center for Nanoscale Systems), ten cycles of the reaction were performed in the empty chamber (process details are provided below). This clears residual gas in the lines. Residual gas was observed to cause higher pressure peaks during the first few cycles of ALD, which could potentially result in more material being deposited in the first few cycles than expected. It also allows time for the chamber to cool to a steady temperature. ALD is performed very close to the melting temperature of the PCTEM, so ensuring a steady temperature is reached before the
membranes are inserted is essential. If the chamber temperature fluctuates to 133°C, the membranes will melt, plugging all of the PCTEM pores.

For ALD, membranes were secured to glass slides at four points using small pieces of Kapton tape (McMaster-Carr). It should be noted that the membranes were not taped along the edges to seal them to the slide. The reason for this is that when sealed along the edges, precursor gases still permeate the membrane through the pores, which would create a pocket of gas between the membrane and the glass slide. The discharge of gas from this cavity can take longer than the charging time. If gas remains in this cavity when the next precursor is cycled, a reaction will occur in the cavity, depositing many layers of material on the membrane and possibly plugging the support pores.

The membranes on glass slides were placed in the ALD chamber and the system pumped to a base pressure of approximately 200 mTorr with a background nitrogen flow rate of 20 SCCM.

Two different ALD materials were used in the experiments, alumina and hafnia. For alumina, the precursor gases are water and trimethyl aluminum (TMA). For hafnia the precursor gases are water and tetrakis(dimethylamino)hafnium(IV) (TDMAH). The process parameters are given in Table 6-1.

Figure 6-4. ALD reactions. a, Alumina. b, Hafnia.
Table 6-1. ALD process parameters.

<table>
<thead>
<tr>
<th>ALD material</th>
<th>Temperature (°C)</th>
<th>Precursor 1</th>
<th>Precursor 2</th>
<th>Precursor 1 pulse time (s)</th>
<th>Precursor 2 pulse time (s)</th>
<th>Wait time between pulses (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alumina</td>
<td>125</td>
<td>water</td>
<td>TMA</td>
<td>0.025</td>
<td>0.3</td>
<td>50</td>
</tr>
<tr>
<td>hafnia</td>
<td>130</td>
<td>water</td>
<td>TDMAH</td>
<td>0.015</td>
<td>0.015</td>
<td>70</td>
</tr>
</tbody>
</table>

Water vapor was released into the chamber in a brief pulse. This was followed by a long wait period to clear the chamber of non-adsorbed water. Then, the second precursor was released, with another long wait period following. The pulse and wait times are given in Table 6-1. This was repeated for the desired number of cycles, which was usually between 10 and 200. On a silicon wafer, alumina is deposited at a rate of approximately 1.1 Å/cycle whereas hafnia is deposited at 0.95 Å/cycle.

6.3.2 ALD formation on graphene

Alumina ALD was performed on graphene over 1.0 μm pore PCTEMs for different numbers of cycles. The resulting structure was examined by SEM imaging (Fig. 6-5). The ALD process deposits material in small islands and long strands on the graphene, presumably covering defect sites. With 50 cycles of deposition (Fig. 6-5c,d), the size of the small islands of materials is larger than 15 nm, which should cover most intrinsic defects (Fig. 4-3). For 100 cycles and less (Fig. 6-5e,f), the fraction of graphene area covered by ALD material is less than 50%, leaving most of the graphene area available for selective nanopores to be created.

By 150 cycles (Fig. 6-5g,h), most of the graphene area is covered in the ALD material. Comparing Fig. 6-5e,f to g,h, it appears that the lateral growth of ALD material from nucleation sites is more rapid than the growth measured on silicon. Thus, although the spacing between
Figure 6-5. SEM images of Al$_2$O$_3$ ALD on graphene on 1.0 μm pore PCTEMs at 125°C for a,b, 0 cycles, c,d, 50 cycles, e,f, 100 cycles, and g,h, 150 cycles.
nanometer-scale intrinsic defects in this CVD graphene is larger than 70 nm, lateral ALD growth from these nucleation sites can result in complete coverage of the material over graphene in a small number of deposition cycles (Fig. 6-5g,h). This could obstruct selective nanopore creation in the membrane.

This lateral growth is further illustrated in Fig. 6-6. This figure depicts ALD on graphene over a 10 nm pore PCTEM (Fig. 6-6b) and over an 80 nm pore PCTEM (Fig. 6-6c,d). In both images, no PCTEM pores are visible beneath the graphene, suggesting that they have been covered by the ALD material. In Fig. 6-6d, even though only 40 cycles of material were deposited, there are areas where lateral growth is approximately 100 nm.

![Figure 6-6. SEM images of ALD on one layer graphene on PCTEMs. a,b, 150 cycle Al₂O₃ at 125°C on 1.0 μm pore PCTEM (a) and 10 nm pore PCTEM (b). c,d, 40 cycle HfO₂ ALD on 80 nm pore PCTEM.](image)
On the 80 nm pore membrane, ALD material forms in ~100 nm circles in several places directly over pores in the membrane (Fig. 6-6d). They appear to be growing inward and outward from the graphene over the edge of the support pore. This suggests that ALD also preferentially deposits material on graphene over the support pore edge. Consequently, even a small number of cycles of ALD on graphene over small diameter support pores can completely obstruct the available graphene area. This is an important consideration if ALD is used to seal intrinsic defects on membranes with small support pores, which may be selected to isolate defects.

*SEM Methodology*

SEM images presented in Ch. 6-8 were performed with an FEI Helios Nanolab DualBeam 600 at 2 kV, 86 pA, in immersion mode, employing an Everhart-Thornley detector. Carbon tape was used to make a conductive path from the graphene to the SEM stub.

### 6.3.3 ALD effectiveness

To test that the ALD material deposited on the membrane is impermeable to gases, the process was performed on a 10 nm pore PCTEM without graphene (Fig. 6-7a). As material is deposited, it reduces the pore diameter, at least at some locations. Flow rates were measured through membranes with different numbers of cycles of ALD, and it was found that the flow rate decreases as the number of cycles increases, with a significant drop above approximately 50 cycles, where the pore is expected to be close to completely obstructed. This indicates that the deposited material does form a barrier to gas permeation.

The resistance of the ALD material to oxygen plasma etching, a method of selective nanopore generation explored in Ch. 8, was also tested. Figure 6-7b shows the results of plasma etching graphene over a 10 nm pore PCTEM with alumina deposited over top. Figure 6-6 suggests that the ALD material completely obstructs the graphene over these small pores. As a result, it
protects the graphene from being destroyed by 1 min of plasma exposure (Fig. 6-7b), which is sufficient time to completely destroy graphene on PCTEMs that has not had ALD performed on it, as shown in Ch. 8. However, at 3 min of exposure, the plasma has significantly damaged the membrane (Fig. 6-7b). Although these results suggests that the ALD material can withstand some oxygen plasma exposure, it is unclear how much exposure could be endured by a smaller amount of material that does not completely obstruct the support pores.

### 6.4 Tear sealing

Larger micron-scale tears will not be sealed by the small thickness of ALD material deposited. To seal these defects, methods are considered in which the graphene membrane is exposed to precursors on either side (Fig. 6-8). These precursors will not interact in areas where graphene is present, but will meet in areas where there are gaps in the graphene coverage. The precursors react there to form a solid material that plugs the tear (Fig. 6-3c). This approach also
has the potential to seal relatively large intrinsic defects in graphene. Smaller intrinsic defects will obstruct precursor interaction, preventing material plugs from forming over them.

6.4.1 Interfacial polymerization

The first type of reaction considered is interfacial polymerization. Interfacial polymerization is a type of polymer formation reaction that occurs at the interface of two solutions. By separating the two solutions with a graphene membrane, the precursors will come into contact at sites with sufficiently large tears, resulting in the formation of a polymer plug.

Interfacial polymerization methodology

Prior to interfacial polymerization, the graphene on PCTEM is heated to 115°C for 12 h to promote adhesion between the graphene and support. The membrane is then exposed to aqueous hexamethylenediamine (HMDA, 5 mg HMDA per mL of 0.05 M sodium bicarbonate solution) on the graphene side in a 5 mL jacketed Franz cell (PermeGear). The solution does not penetrate the pores because the 200 nm pore, PVP-free PCTEM is hydrophobic. The other side of the membrane

Figure 6-8. Illustration of tear sealing by interfacial polymerization. The membrane is exposed to precursors (hexamethylenediamine in water and adipoyl chloride in hexane) on either side. The solutions form an interface where there are tears in graphene and react to form a polymer plug.
is then exposed to adipoyl chloride (APC, 4 µL per mL of hexane). APC wets the PCTEM pores and meets the HMDA, where they react to form a nylon-6,6 plug (Fig. 6-8, 6-9a).

\[
\text{Cl-C-(CH}_2\text{)}_4\text{-C-Cl} + \text{H}_2\text{N-(CH}_2\text{)}_6\text{-NH}_2 \rightarrow \text{(-C-(CH}_2\text{)}_4\text{-C-NH-(CH}_2\text{)}_6\text{-NH-)} + \text{HCl} \quad (6-1)
\]

The reaction was allowed to proceed for 1 h, with Parafilm used to seal the reaction cell to prevent evaporation. Upon completion, the APC side of the membrane is rinsed seven times with hexane and seven times with ethanol. A column of ethanol is left in the Franz cell when the membrane is removed. The membrane is then rinsed by submersion in three ethanol baths for 5 min each before being air dried.

**Interfacial polymerization effectiveness**

Gas flow rates through 200 nm PCTEMs with and without graphene, before and after the interfacial polymerization reaction (IP), are presented in Fig. 6-10a. Interfacial polymerization on the PCTEM without graphene significantly reduces the gas flow rate. However, a small residual flow rate remains. This may be due to flow through the polymer that forms in the pores, which will have an inherent permeance.

On the membranes without IP, graphene reduces the flow rate compared to a bare PCTEM by blocking many of the support pores (Fig. 6-10a-c). However, after IP, the membrane with

![Figure 6-9. Tear sealing experimental setup. a, Interfacial polymerization. b, Ammonium chloride precipitation.](image)
graphene has a higher flow rate than the bare PCTEM (Fig. 6-10a). This is likely a result of the inherent gas permeability of the nylon that is formed. On the PCTEM without graphene, IP results in polymer forming in all of the support pores (Fig. 6-10d). When IP is performed on the graphene membrane, polymer only forms in pores without graphene coverage (Fig. 6-10e). The graphene that remains still has open intrinsic defects, which are gas permeable. As a result, the flow rate through this membrane is higher than that of the PCTEM without graphene, after IP.

Interfacial polymerization reduces leakage through the graphene membrane, indicating that low permeance polymer is plugging areas with large tears. Furthermore, higher flow rates are observed on membranes with graphene than without, after interfacial polymerization. This is attributed to flow through defects in the graphene, not covered by polymer, and providing evidence that the IP process is not blocking areas of the membrane with graphene.

It is possible that the polymer precursors will adsorb on small nanopores in graphene. Performing the polymerization reaction before selective nanopore creation would prevent this. However, this requires the polymer to be resistant to the etchants used in nanopore creation. Figure
6-11 shows gas flow rates after etching PCTEMs without graphene using potassium permanganate, UV-ozone, and oxygen plasma, selective pore creation etchants considered in Ch. 8.

Resistance to UV-ozone and oxygen plasma was tested on 200 nm pore PCTEMs without graphene. UV-ozone exposures that destroy graphene are on the order of 75 min (Ch. 8). The polymer permeance is almost unaffected by etching of this duration (Fig. 6-11b). Oxygen plasma etching destroys graphene in 1-2 min (Ch. 8). Although oxygen plasma exposures of ~25 min cause significant damage to the nylon, the polymer maintains low permeance over the ~2 min exposure required for selective pore creation (Fig. 6-11c).

Resistance to potassium permanganate etching was tested on bare 10 nm pore PCTEMs. Figure 6-11a shows an increase in flow rate at early potassium permanganate etch times, followed by a constant, still relatively low, flow rate. This flow rate is retained for 1 h, the maximum typical potassium permanganate etch time for graphene (Ch. 8). Etching a 10 nm pore PCTEM without graphene also results in an increase in flow rate (Fig. 6-11a). This suggests that the potassium permanganate etchant is either opening PCTEM pores initially blocked in the membrane, or enlarging the support pores without disrupting most of the polymer plugs. These results indicate that the polymer can tolerate up to 1 h of potassium permanganate etching without loss of gas

![Figure 6-11. Durability of interfacial polymer plug to various pore creation etch techniques. a, Potassium permanganate etching of a 10 nm pore PCTEM without graphene, with and without IP. b, UV-ozone etching of 200 nm pore PCTEM without graphene and with IP. c, Oxygen plasma etching of two 200 nm pore PCTEM without graphene and with IP.](image-url)
barrier properties. PCTEM etching should not be a significant issue on larger, 200 nm pore PCTEMs.

Other observations

It should be noted that the gas flow rate reduction due to interfacial polymerization was insensitive to the reaction conditions. Specifically, reaction times of 2 min to 2 h, HMDA concentrations of 5 mg/mL to 50 mg/mL, and APC concentrations of 4 μL/mL to 8 μL/mL did not significantly affect gas flow rates after polymerization.

An interfacial polymerization reaction for aromatic nylon was also attempted. In this approach, m-phenylenediamine takes the place of HMDA (5 mg per mL of 0.05 M aqueous sodium bicarbonate solution) and 1,3,5-benzenetricarbonyl trichloride takes the place of APC (4 μL per mL of hexane). The reaction was allowed to proceed for 2 min. Similar gas flow rate reduction results were obtained as for the aliphatic nylon reaction. The nylon-6,6 reaction was selected for experiments because it has better resistance to the potassium permanganate etchant used in selective pore creation in Ch. 8.

When the interfacial polymerization procedure is performed on hydrophilic membranes, the HMDA appears to wet the membrane, flowing through before the APC is added. This results in a visible coating of polymer on the APC side of the membrane. This polymer obstructs the entire membrane, and although it flakes off when the membrane is washed, polymer has not formed in the support pores beneath tears in graphene.

Interfacial polymerization was also performed on a 20 nm isotropic pore anodized aluminum oxide (AAO) membrane, described in Ch. 7. The reduction in flow rate was less than 50% after the IP reaction, compared to 98.5% achieved on 200 nm PCTEM. No polymer film was visible on the surface following the reaction. It is not clear whether the precursors had sufficient
interaction to form polymer plugs, or whether the reaction occurred in the pores or at the surface. However, it is possible that the gas flow resistance of the nylon is similar to that of the relatively high resistance AAO support pores, such that it is not effective at sealing gas flow.

6.4.2 Ammonium chloride precipitation

Another method considered for plugging support pores behind tears in graphene was to precipitate ammonium chloride into the pores.

Ammonium chloride precipitation methodology

The membrane was mounted in a 5 mL jacketed Franz cell (PermeGear). The 5 mL side was filled with 36% hydrochloric acid to below the base of the built-in spout (Fig. 6-9b). Evaporation of hydrogen chloride gas exposed the membrane to this precursor. The upstream side was fitted with a tube connected to a valve that could flow nitrogen at a regulated pressure, or ammonia in a nitrogen carrier gas by bubbling nitrogen through 30% ammonium hydroxide. The nitrogen source was attached to a regulator with 0.01 psi precision.

During the reaction, nitrogen was flowed through the membrane for 2 min at 5 psi upstream pressure to clear hydrogen chloride from the membrane pores. The valve was then turned to bubble 5 psi nitrogen through the ammonium hydroxide solution, flowing ammonia through the membrane. The reaction was allowed to proceed for 20 min before turning off the ammonia source, flowing nitrogen for 2 min, then turning off the nitrogen flow and removing the membrane. The reaction

\[
\text{NH}_3(g) + \text{HCl} (g) \rightarrow \text{NH}_4\text{Cl} (s) \quad (6-2)
\]

occurs, precipitating solid onto the membrane.

This reaction occurs even for small concentrations of the gas precursors, so choosing appropriate reaction conditions are important to ensure that the precipitate forms in the support
pores, not on the surface. This would allow the membrane reaction to plug pores beneath tears in graphene, without blocking flow through the entire membrane.

*Ammonium chloride plug effectiveness on PCTEMs*

An upstream pressure of 1 psi was found to be insufficient to prevent ammonium chloride deposition on the upstream side of the PCTEM. At this pressure, significant diffusion of HCl (g) to the upstream side of the membrane occurs, precipitating ammonium chloride, which is then filtered through the PCTEM, depositing on the surface of the membrane in a visible layer. At 5 psi, no significant precipitate formation is observed on either side of the PCTEM (Fig. 6-12a-c). Only a few small crystals are observed, but the support pores are not covered on the surface. At this flow rate, HCl (g) diffusion to the upstream side of the membrane is low. Precipitate formed downstream will flow out of the cell or fall to the HCl (aq) surface, rather than depositing on the membrane.

At this pressure, there is a sufficient balance between HCl (g) diffusion into the pores and convective NH₃ flow through the pores to reduce the flow rate through the membrane by 90% (Fig. 6-12d) without precipitate visible on the membrane surface by eye or SEM (Fig. 6-12a-c). This suggests that precipitate is forming in the pores, but that the structure formed is more gas permeable than the nylon formed by interfacial polymerization.

*Ammonium chloride plug effectiveness on AAOs*

When the ammonium chloride precipitation reaction was performed on 20 nm pore, 50 μm thick AAO membranes (InRedox, isotropic membranes), the flow rate decreased by approximately 99% (Fig 6-12d) without precipitate formation on either side (Fig. 6-12e,f). Control experiments were performed without HCl. In the first experiment, nitrogen was flowed through the membrane for 6 h to see if the flow rate reduction was resulting from particles in the nitrogen source
obstructing the AAO pores. The results show no significant change in flow rate (Fig. 6-12d). In the second control experiment, NH\textsubscript{3} was flowed through the membrane for 2 h without HCl on the other side. The flow rate decreased by more than 99\% (Fig. 6-12d). This indicates that the reduced flow rate for the AAO membranes is not resulting from ammonium chloride precipitation.

In this process, ammonia may be dissolving in water that has condensed in the AAO pores. Alumina is highly soluble in ammonia\textsuperscript{102}, which could lead to erosion of the pore wall. The dissolved alumina may be forming a solid plug in the AAO pore after the water and ammonia evaporate. If the AAO pores can be plugged by ammonia exposure without damaging the graphene or underlying AAO surface, and without connecting support pores, it may still be possible to use this approach to seal the AAO support. However, this has not been investigated further.

**Figure 6-12.** Ammonium chloride sealing. a, b, SEM images of NH\textsubscript{3} exposed side of 30 nm pore PCTEM. c, SEM images of HCl exposed side of 30 nm pore PCTEM. d, Flow rate measurements, normalized by flow rate through untreated membrane. e, SEM image of NH\textsubscript{3} exposed side of 20 nm pore AAO. f, SEM image of HCl exposed side of 20 nm pore AAO.
6.5 Conclusions

Gas permeable defects in graphene membranes can completely compromise membrane selectivity. In this chapter, methods to reduce the defect density in graphene membranes have been explored. A method to use gas flow rate measurements to compare initial graphene quality and compatibility with the transfer process was established and used to select the most suitable graphene for membrane applications. Using multi-layer graphene was shown to be a viable method for leakage sealing. Methods to seal defects in single-layer graphene were also investigated. It was shown that atomic layer deposition can seal nanometer-scale intrinsic defects in graphene to gases while leaving pristine areas of graphene uncovered and available for selective nanopore creation. It was shown that interfacial polymerization of single-layer graphene membranes can partially seal micrometer-scale tears in graphene to gas flow. These methods of fabricating lower defect density graphene membranes brings the technology closer to achieving selective transport on a macroscopic scale and to a commercial product.
Chapter 7

Support membrane tuning

Tears and intrinsic defects not eliminated or sealed can cause leakage to dominate gas transport through graphene membranes. However, as discussed in Ch. 5, an optimized support membrane beneath the graphene can mitigate the effects of these defects. The resistance to gas flow of the support membrane should be well matched to the selective pore resistance to minimize the impact of leakage through micron-scale tears. Furthermore, the characteristic length scale of the support, either the support pore diameter or dense layer thickness, should be sufficiently small so as to isolate intrinsic defects such that they do not compromise large areas of the membrane. Support membrane design and fabrication is the subject of this chapter.

7.1 Support membrane resistance tuning

For visualization, Fig. 7-1 presents a simplified comparison of the graphene resistance, resulting from selective nanopores and intrinsic defects, to the resistance of support membranes of different structures.
The graphene resistance \( R \) [Pa-s/mol] to gas flow due to selective pores in the area of graphene over a support pore of a given diameter was calculated for various assumed values of the graphene permeance, \( p \) [mol/m\(^2\)-s-Pa] by,

\[
R = \frac{4}{\pi p D_{\text{supp}}^2} \quad (7-1)
\]

where \( D_{\text{supp}} \) [m] is the support pore diameter. Values of possible selective pore permeance between \( 2 \times 10^{-6} \) and \( 2 \times 10^{-4} \) mol/m\(^2\)-s-Pa were selected based on reported single pore measurements\(^{33}\) and simulations\(^{36-38,59}\) using measured created pore densities.\(^{82,84}\) The resistance due to selective nanopores scales as \( R \sim D_{\text{supp}}^{-2} \), because the number of selective nanopores in the graphene over a support pore is proportional to the area of the support pore.

The resistance of graphene due to intrinsic defects was calculated from the effective intrinsic porosity \( \eta_{\text{eff}} \) using the equation for high Knudsen number gas effusion through an orifice,\(^{80}\)

\[
R = \frac{\sqrt{2 \pi MRT}}{\eta_{\text{eff}}} \cdot \frac{4}{\pi D_{\text{supp}}^2} \quad (7-2)
\]

Here, the effective intrinsic porosity is the open area fraction due to defects in graphene, excluding those defects with lower resistance than the support pores. Smaller support pore diameters result in higher support pore resistances. When a defect’s resistance is lower than that of the support, it effectively acts as an open area of graphene. Thus, it is treated as producing lower graphene coverage rather than higher intrinsic porosity. As seen in the Fig. 7-1d, defect isolation by choosing a small support pore diameter has a significantly larger relative effect on intrinsic porosity than on graphene coverage. The largest defect size \( D_{\text{defect}} \) included in the intrinsic defect resistance calculation is determined by equating the expressions for the AAO support pore resistance (given later in Eq. 7-9) to the resistance to gas flow of a small orifice.
The effective porosity of pores less than this defect size was estimated from the measured size distribution of defects in CVD graphene (Fig. 4-3). This was done by obtaining a fit to the cumulative probability distribution of measured defect size (Fig. 7-1b). An exponential fit was used,

\[
F(D) = 1 - e^{-aD} \tag{7-5}
\]

where \(D\) is the defect size, \(F\) is the cumulative probability, that is the probability that the pore size is less than \(D\), and \(a = -0.1802\) nm\(^{-1}\) is the fitting parameter obtained. The approximated defect size distribution, \(P(D)\), is then,

\[
P(D) = \frac{dF}{dD} = ae^{-aD} \tag{7-6}
\]

and the fraction of the total defect area corresponding to defects of diameter less than \(D\) is,

\[
\frac{\eta_{eff}}{\eta} = \int_{0}^{D} \frac{\pi x^2 P(x) \, dx}{\int_{0}^{\infty} \pi x^2 P(x) \, dx} = 1 - \frac{1}{2}e^{-aD}(a^2D^2 + 2aD + 2) \tag{7-7}
\]

where \(\eta\) is the overall intrinsic porosity of the graphene, including all pores. Substituting \(D_{defect}\) in Eq. 7-4 for \(D\) in Eq. 7-7 gives the effective intrinsic porosity for a given support pore diameter (Fig. 7-1c). This ratio is used in Eq. 7-2 to calculate the resistance due to intrinsic defects in Fig. 1a.

Note that the resistance due to intrinsic defects depends on the defect isolation ability of the support. The plotted intrinsic defect resistance in Fig. 7-1a is for the AAO support. This curve will differ for the PCTEM because the defect size cut-off will be different, resulting in different
effective intrinsic porosities for a given support pore diameter, and hence a different average intrinsic defect resistance.

The estimated graphene resistance due to intrinsic defects is plotted in Fig. 7-1a for intrinsic porosities of 0.03-0.7%, typical of CVD graphene (Fig. 6-1). For large support pores (~$10^{-6}$ m),

**Figure 7-1.** a, Scaling of the flow resistance of graphene. Resistances are for a support pore or graphene area over a support pore of the plotted diameter. The resistance of graphene due to selective pores and intrinsic defects are shown for different values of intrinsic porosity and permeance due to selective pores, respectively. Isotropic PCTEM (polycarbonate track etched membrane), isotropic AAO (anodic aluminum oxide membrane), PDMS layer (polydimethylsiloxane, with different layer thicknesses indicated), and packed sphere resistances are computed from models discussed in this chapter. Here, the term isotropic is used to mean constant pore diameter throughout the membrane thickness. The plotted resistances are for helium. b, Cumulative probability distribution of intrinsic defect sizes, measured from STEM images of graphene, and corresponding exponential fit (Eq. 7-5). c, Reduction of effective intrinsic porosity ($\eta_{\text{eff}}$) with support pore diameter ($D_{\text{supp}}$). Intrinsic defects with gas resistance less than the support pore resistance become tears, effectively reducing the graphene coverage while no longer contributing to the effective intrinsic porosity. The ratio of effective intrinsic porosity to the actual intrinsic porosity of the graphene ($\eta$) is plotted (Eq. 7-7,7-4). d, Percentage change in graphene coverage and effective intrinsic porosity as support pore size is reduced. Reducing the pore size raises the fraction of intrinsic defects that have comparable gas flow resistance to that of the support pore. Consequently, these defects behave as large tears, reducing coverage, rather than small defects, reducing intrinsic porosity.
the intrinsic defect permeance may be higher than the selective pore permeance, preventing overall membrane selectivity. However, smaller pore diameters isolate defects, creating effectively lower intrinsic porosities and raising their resistance to much higher than the selective pore resistance. This reduced effective porosity may also explain why model predictions of intrinsic porosity on 200 nm PCTEM supports (Fig. 6-1) are lower than on 1.0 μm supports (Fig. 4-6). Furthermore, higher intrinsic defect resistance is essential to selective membrane design, as it ensures that transport through selective pores will be greater than leakage through intrinsic defects, which would otherwise prevent selective gas permeation. However, leakage through micron-scale tears can still be significantly higher than flow through selective pores, necessitating support pore resistance matching.

Ideally, the support membrane resistance will be approximately matched to the selective nanopore resistance. This would make the contribution of flow through support pores with selective graphene approximately equal to the leakage flow through open support pores. Significantly lower support resistance would cause leakage to dominate whereas significantly higher support resistance would inhibit flow in the support pore behind selective graphene. Thus, the blue band in Fig. 7-1a is the approximate design goal for the support pore resistance.

7.2 Small pore diameter commercial supports

As predicted in Ch. 5, smaller diameter support pores have the benefit of isolating nanometer-scale intrinsic defects to the graphene over a small fraction of the support pores. The experiments discussed in Ch. 3 were for graphene over PCTEMs with 200 nm and 1000 nm pores, but PCTEMs are commercially available with pore sizes as small as 10 nm. Choosing smaller support pore sizes should also be a method of support pore resistance tuning. For relatively large
support pore diameters, for which \( Kn \ll 1 \), continuum hydrodynamics applies and the support pore resistance is expected to be given by the equation for Poiseuille flow (Box 1-1),

\[
R = \frac{128 \mu L \bar{R} T}{\pi D_{\text{supp}}^4 P}
\]  

(7-8)

where each of the above parameters is defined in Box 1-1. For relatively small support pore diameters, for which \( Kn \gg 1 \), the support pore resistance is expected to be given by the equation for Knudsen diffusion (Box 1-1),

\[
R = \frac{3L}{\pi D_{\text{supp}}^3 \sqrt{2 \pi M \bar{R} T}}
\]  

(7-9)

At intermediate pore sizes, where \( Kn \approx 1 \), these limits are inaccurate. However, the support pore resistance can be estimated from numerical solutions to the Boltzmann transport equation. \(^{103-105}\) A solution to the linearized Boltzmann equation with the BGK approximation for the collision operator, integrated over the finite pore length, was used to estimate the resistance of PCTEMs with cylindrical pores\(^{104}\) in Fig. 7-1 (isotropic PCTEM data). These calculations were performed for an upstream pressure of 1 atm and vacuum downstream.

The fit to computed isotropic PCTEM support resistance (corresponding dashed line in Fig. 7-1) shows approximate \( R \sim D_{\text{supp}}^{-3} \) scaling, expected for Knudsen diffusion. The selective pore resistance scales as \( R \sim D_{\text{supp}}^{-2} \), and thus, if the support pore diameter, \( D_{\text{supp}} \), is reduced, the support resistance will match the graphene resistance. This is shown to occur for 10 nm pore PCTEMs, where the isotropic PCTEM resistance curve crosses the selective pore resistance band. By this reasoning, choosing a small support pore diameter should both isolate defects and match the support resistance to the graphene resistance. The approach of using a small diameter pore PCTEM to optimize the support membrane is discussed below.
7.2.1 Small pore diameter PCTEM graphene transfers

The reason larger support pores were selected for previous experiments (Ch. 3) is that standard PCTEMs in those sizes can be purchased without PVP (polyvinylpyrrolidone) coatings. Smaller diameter PCTEMs are PVP coated to make them hydrophilic, facilitating water filtration. However, the graphene transfer described in Section 3.2 is not compatible with hydrophilic support membranes; during copper etching, ammonium persulfate tends to wick in between the graphene and the support, either from the edges of the copper or through areas where the copper has been fully removed. This prevents adhesion between the graphene and PCTEM.

Custom made PVP-free 10 nm pore PCTEMs (SPI) were obtained and graphene was successfully transferred onto them by a slightly modified procedure (Fig. 7-2, 2011 PCTEM); instead of allowing the PCTEM to overhang the graphene on copper during etching, the PCTEM was cut into a square slightly smaller than the copper square so that no PCTEM contacted the APS at the start of the etching step. This further discouraged wicking of the APS between the graphene and PCTEM. However, subsequent batches of the PVP-free 10 nm pore PCTEMs from SPI and Sterlitech were more hydrophilic and not amenable to graphene transfer (Fig. 7-2a, 2013 PCTEM).

Other methods to transfer graphene to small diameter PCTEMs

Various methods of PCTEM modification were attempted to improve transfer quality. Depositing 20 cycles of HfO$_2$ by ALD on the PVP-free 10 nm pore PCTEM did not measurably reduce the gas permeance of the membrane, but improved its hydrophobicity sufficiently (Fig. 7-2b,c) to allow high coverage graphene transfers (Fig. 7-2a, 2013 PCTEM with ALD in 2013). This method was also unreliable for consistently obtaining high coverage (Fig. 7-2a, 2013 PCTEM with ALD in 2014). Another illustration of the batch to batch variability in PCTEMs is shown in Fig. 7-3. For a period of time shortly after Sterlitech changed their pore etching procedure, the 200 nm
pore PCTEMs they supplied had large open cavities on one side of the membrane, rather than maintaining separate cylindrical pores throughout the membrane thickness.

Membrane silanization methods to increase hydrophobicity were also attempted. In the first method, the bare PVP-free 10 nm pore PCTEMs were exposed to chlorotrimethylsilane (200 μL, Sigma-Aldrich) for 5 min in a petri dish (150 mm) under ambient conditions. In the second method, the membranes were exposed to (heptadecafluoro-1,1,2,2-tetra-hydrodecyl) trichlorosilane under vacuum for 2 h, then the silane was removed and the membrane was left under vacuum for 12 h before finally being baked at 120°C for 3 h. These methods did make the PCTEMs hydrophobic and allowed for graphene transfer, but plugged pores in the membrane, reducing the flow rate through the membrane without graphene by ~75%.

Methanol rinsing the PCTEMs (2 h, stir table at 150 rpm) was also attempted to remove PVP from standard membranes before graphene transfer. This approach did improve graphene transfer quality, but did not result in consistently high coverage. Other membranes were treated...
with didecylamine (15 mg/mL in ethanol, 1 h, stir table at 150 rpm, then ethanol rinsed) to make them more hydrophobic. This approach was not successful for 10 nm pore PCTEMs.

During graphene transfer to small diameter pore PCTEMs, bubbles formed by etching in ammonium persulfate (APS) have a greater tendency to remain stuck to the copper. When the copper is etched away, the graphene curls up around the bubbles. It is postulated that for larger pore diameter supports, the gas passes through tears in the graphene and through the support pores, possibly damaging the graphene in the process. When the support pores are smaller, this tendency is reduced, so larger gas bubbles form on the membrane. Etching under a higher pressure (45 psi) nitrogen environment reduced the size of the bubbles, reducing the area of damaged graphene they caused. Etching in APS with constant agitation from a magnetic stir bar also helped to dislodge bubbles before the copper was fully etched.

Figure 7-3. Variability in commercial PCTEMs. SEM images of 200 nm pore PCTEM (Sterlitech) cross sections. The images show a stack, from right to left, of PDMS, graphene, and a PCTEM. a,b, PCTEMs purchased in 2013. c,d, PCTEMs purchased in 2014. Membranes were sputter coated with 2 nm of 80% / 20% Pt / Pd for imaging.
None of these approaches provided the level of graphene coverage obtained on PVP-free 10 nm pore PCTEMs from the original 2011 batch. The experiments presented for 10 nm pore PCTEM are from that batch.

7.2.2 Small pore diameter PCTEM resistance

The reliability of graphene transfers to small diameter pore PCTEMs was not a significant limitation, because further analysis showed that they did not provide adequate resistance matching. Although the predicted PCTEM resistance (Fig. 7-1, isotropic PCTEM) has $R \sim D_{\text{supp}}^{-3}$ scaling and is approximately matched to the selective pore resistance for 10 nm diameter support pores, the measured resistance (Fig. 7-1, measured PCTEM) has $R \sim D_{\text{supp}}^{-2}$ scaling. Consequently, reducing the support pore diameter does not change the ratio of selective pore resistance to support pore resistance. Although reducing the PCTEM pore size achieves the desired intrinsic defect isolation, it does not provide support resistance matching.

To understand this unexpected resistance scaling, gas flow rate measurements for PCTEMs of different diameters are compared to model predictions of Navier-Stokes (continuum Poiseuille flow) and linearized Boltzmann BGK\textsuperscript{103–105} (Bhatnagar–Gross–Krook) in Fig. 7-4a,b. Both models give reasonable results for large pore diameters (~1 μm). However, both models under-predict permeance by orders of magnitude as the pore size is reduced to 10 nm.

In the latter model, the Boltzmann equation for particle transport through a cylindrical pore is solved for infinitesimal pressure differences. These solutions are used to construct approximations to the flow field in pores under the action of finite pressure differences to obtain the mass flow rate. In this work, the BGK approximation is used for the collision operator, in which the collision operator drives the system to local equilibrium at a rate that is proportional to
the deviation therefrom. The proportionality constant in this approximation, the inverse of the relaxation time, is selected to match the gas viscosity to that of Chapman-Enskog theory.

Figure 7-4a,b also presents solutions to the linearized Boltzmann BGK model for an accommodation coefficient of $\alpha = 0.6$, in addition to the standard $\alpha = 1.0$ solution. The accommodation coefficient quantifies the fraction of diffuse rather than specular reflections of molecules colliding with the pore wall. Comparison of the measurements to this solution was performed to assess whether such molecule-pore interactions could account for the discrepancy. While the flow rates for $\alpha = 0.6$ are shifted compared to $\alpha = 1.0$, they do not capture the different permeance-diameter scaling measured on the PCTEM.

The reason for the anomalous flow rate scaling was revealed by cross-section SEM images of the small diameter PCTEM pore structure (Fig. 7-5a). Although these membranes have the manufacturer specified pore diameter on the surface, the pore quickly opens to a much larger diameter pore in the bulk of the membrane. The image in Fig. 7-5a shows that the 30 nm pore PCTEM opens into ~100 nm diameter pores in the bulk of the PCTEM. PCTEM pore etching is designed to create such a structure; the small surface diameter provides small particle

![Figure 7-4. Gas permeance measurements of bare PCTEMs of different pore diameters. a, Measured permeance compared to predictions from Navier-Stokes and linearized Boltzmann BGK for accommodation coefficients, $\alpha$, of 1.0 and 0.6. b, Corresponding flow rate ratios. c, Comparison of measurements to model fit of the pore diameter in the bulk of the PCTEM to match measured flow rates.](image-url)
filtration while the large bulk diameter ensures high flow rates. Although this structure is good for particle filtration, it causes the graphene and support resistance to have the same scaling with pore diameter.

To further test this finding, a least squares fit was performed to find the support pore diameter such that the flow rates predicted by the linearized Boltzmann BGK model with $\alpha = 1.0$ matched the measured flow rates. The resulting fit and predicted bulk diameter are plotted in Fig. 7-4c. In this plot, surface diameter is the manufacturer specified PCTEM diameter whereas bulk diameter is the pore diameter obtained by fitting to the flow rate measured on the membrane. Greater deviation between bulk diameter and surface diameter occurs for smaller pore sizes.

Figure 7-5. Structure of standard porous membranes considered as a support layer for graphene. a, PCTEM, b, AAO, c, PVDF. Top row shows a sketch of the membrane cross section (not to scale). Middle row shows SEM images of the top surface. Bottom row shows cross section images of the membrane. Note that in the cross section images, the top surface is visible in the upper portion of the images. Membrane were sputter coated with 2 nm of 80% / 20% Pt / Pd for imaging.
Furthermore, the predicted bulk diameter for 30 nm PCTEMs are in reasonable agreement with those observed from cross-section imaging (Fig. 7-5a).

From this analysis, it was concluded that small diameter pore commercial PCTEMs would not give the desired selective nanopore resistance matching.

### 7.2.3 Other small pore diameter membranes

The PCTEM structure, having a thin active layer with relatively small pores and a thick support layer with large pores, is a common commercial membrane design (Fig. 7-5). Whatman 20 nm anodic aluminum oxide (AAO) membranes have a 0.1-1 μm layer with 20 nm pores that open into 200 nm pores for the remainder of their 60 μm thickness (Fig. 7-5b). Similar to the PCTEMs, this is undesirable for resistance matching.

Polyvinylidene difluoride (PVDF) membranes have a thin, dense skin layer, with a lower density bulk (Fig. 7-5c). For such a structure to provide defect isolation, the thickness of the skin layer needs to be less than the spacing between defects. Graphene transfers to PVDF membranes did not show significant reductions in gas flow compared to the membrane without graphene, indicating that defect isolation was not achieved with this structure.

### 7.3 Support membrane modification attempts

Without an available commercial membrane with the desired pore structure for resistance matching, attempts were made to modify commercial membranes to achieve the required resistance. The two main structures considered were laminate membranes (Fig. 7-6a) and particle filled membranes (Fig. 7-6c).
7.3.1 Laminate support membranes

Laminate support membranes were envisioned as consisting of two PCTEMs, one with a large pore diameter (e.g., 200 nm) with graphene over it, and one with a small pore diameter (e.g., 10 nm). With this structure, the graphene selective pore resistance corresponds to that of the large diameter PCTEM pore, whereas the support pore resistance would be dominated by that of the small diameter support pore. This is the case because the two support membranes have similar thickness (10 µm for the 200 nm pore PCTEM and 6 µm for the 10 nm pore PCTEM), in contrast to the active and support layer structure of commercial membranes, and similar pore density (3×10^8 cm^-2 for the 200 nm pore PCTEM and 6×10^8 cm^-2 for the 10 nm pore PCTEM), meaning

Figure 7-6. PCTEM support modification attempts to tune the gas flow resistance. a, Schematic of stacked PCTEMs of two different pore sizes. b, Gas flow measurements through a PCTEM stack. c, Schematic of particle packing. d, Flow rates measured for membranes with particles in the pores and on the surface of 200 nm pore PCTEMs. Flow rates are normalized by the bare PCTEM flow rate without treatment.

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that it is unlikely for a larger pore to feed into more than a couple of small diameter pores. In this way, the support resistance can be matched to the graphene resistance (Fig. 7-1).

Attempts were made to create the laminate membrane by (1) pressing the two PCTEMs together, (2) sealing the PCTEMs on the edges with epoxy, and (3) gold coating the membranes, exposing one to nonanethiol to form a self-assembled monolayer,\textsuperscript{108,109} and then pressing the PCTEMs together to bond them. Example results are shown in Fig. 7-6b. The flow rates through the membrane with a 200 nm PCTEM over a 30 nm PCTEM were not reduced compared to the 30 nm PCTEM. Since the porosity of the 200 nm PCTEM is approximately 10\%, this suggests that there is leakage between the two membranes. Instead of support pores in the two PCTEMs acting as a series resistance, the two entire PCTEMs are acting in series. Cross-talk between support pores will not achieve the tear isolation intended by the chosen isolated pore support membrane structure.

7.3.2 Particle filled or coated support membranes

Another membrane structure considered was one in which the support pores of a PCTEM were partially filled with particles to increase the resistance of the support pore. An expression derived from the kinetic theory of gases for flow through a packed sphere bed was used to estimate the resistance of this configuration. The resistance of the unfilled portion of the support pore was added in series to that of a packed sphere bed,\textsuperscript{110}

\[
R = \frac{4\sqrt{2\pi MR}}{\epsilon \pi D_{supp}^2} \left( 1 + \frac{3(1 - \epsilon) \varphi q L_{fill}}{2 \epsilon r_{sphere}^4} \right) \quad (7-10)
\]

where \(r_{sphere}\) is the radius of the spheres, \(L_{fill}\) is the length of the support pore filled with spheres, \(\epsilon\) is the open volume fraction, \(\varphi = 2.18\), and \(q = 1.41\). For example, 30 nm spheres filled to 4 \(\mu\)m of the 10 \(\mu\)m long pores, assuming an open volume fraction\textsuperscript{111} of \(\epsilon = 0.38\) should provide a well matched support pore resistance (Fig. 7-1, packed 30 nm spheres).
Vacuum filtration of solutions containing different particles through 200 nm pore PCTEMs was performed in an attempt to obtain the nanoparticle (NP) packed pore structure. Silica nanoparticles (10-20 nm, Sigma-Aldrich) in ethanol, diamond nanoparticles (<10 nm, Sigma-Aldrich) in ethanol, and black ink (70-700 nm particles, 112 Higgins Inks) in water were each filtered through separate membranes. For concentrations or total permeated volumes where a layer of particles did not form on the PCTEM surface, or in which that layer was allowed to flake off, flow rate reductions compared to the initial PCTEM were less than 50% (Fig. 7-6d). These flow rates, being significantly higher than for a support pore packed with particles, suggest that the particles are not forming packed structures within the pore.

Attempts were also made to spray coat particles onto the surface of the PCTEM. A thin layer of particles could increase the support membrane resistance while retaining the tear isolation properties of the underlying PCTEM. Diamond nanoparticles in ethanol and titania nanoparticles in isopropanol (25 nm, 10 mg/mL, Sigma-Aldrich) were spray coated on separate membranes. Again, the flow rate reductions were small (Fig. 7-6d) compared to that required to match the selective pore resistance (Fig. 7-1).

7.4 Dense, permeable polymer film

Another approach to support resistance tuning is to deposit a thin, permeable polymer coating on the membrane (Fig. 7-7a). Choosing a polymer with a suitable permeability, the resistance can be adjusted by changing the thickness of the polymer layer. If the layer thickness is sufficiently smaller than the spacing between the underlying PCTEM pores, tears in the graphene will remain isolated because spreading of the gas flow within the polymer will be insufficient for cross-talk between flows through different PCTEM pores. If the layer is thinner than the spacing
between intrinsic defects, those too can be isolated by localizing the flow in the film. The support PCTEM diameter can also provide intrinsic defect isolation in this configuration.

As a first estimate of the layer thickness required for various polymers, their permeability\textsuperscript{113} was used in a one-dimensional Fickian diffusion model,

\[
L_{\text{polymer}} = \frac{\pi D^2_{\text{supp}}}{4} R \left( \frac{\kappa}{RT} \right)
\]

where \( R \) [Pa-s/mol] is the desired support layer resistance, \( \kappa \) [m\(^2\)/s] is the gas diffusivity in the polymer, and \( \kappa/RT \) [mol-m/m\(^2\)-s-Pa] is the gas permeability in the polymer. The estimated thickness required for various polymers to achieve 1000 times higher resistance than a 200 nm PCTEM pore is shown in Fig. 7-7b. This estimate was used for polymer selection, but a more precise model accounting for gas flow spreading in the polymer film is discussed in Section 7.4.1 and used for resistance estimates.

The estimated layer thickness required for many polymers is too thin to deposit by spin coating (<10 nm). The thicknesses required for Teflon, polymethylpentene, and poly[1-(trimethylsilyl)-1-propyne] are all greater than 100 nm. However, the permeabilities for these polymers are for very high free volume structures, which may be difficult to prepare with thickness of less than even 10 \( \mu \)m.\textsuperscript{114} Polydimethylsiloxane (PDMS) is relatively easy to deposit and requires
a thickness of ~100 nm, which has been achieved by spin coating.\textsuperscript{115} For this reason, PDMS was selected for experiments where resistance tuning is accomplished through use of a polymer layer.

7.4.1 Polymer film resistance model

A more sophisticated model for diffusion in a solid was used to approximate the resistance of PDMS films of different thicknesses. The model is for diffusion in a cylindrical volume (PDMS) with radius \( b \), and zero flux on the circumference (Fig. 7-8a). One surface has a circular center area with radius \( a \) and thickness \( L \), held at constant concentration, \( c_H \), with zero flux elsewhere, while the other is held at constant concentration, \( c_L \). The approximate gas flux through this volume is,\textsuperscript{116}

\[
\frac{J}{\kappa a \Delta c} = \left[ \frac{aL}{\pi b^2} + \frac{2b}{a\pi} \sum_{n=1}^{\infty} \frac{J_1\left(\frac{a\lambda_n}{b}\right) \sin \frac{a\lambda_n}{b} \tanh \frac{L\lambda_n}{b}}{\lambda_n^3 [J_0(\lambda_n)]^2} \right]^{-1} \tag{7-12}
\]

where \( J_0 \) and \( J_1 \) are zeroth and first order Bessel functions of the first kind, \( J \) [mol/s] is the molar flow rate, and \( \lambda_n \) is defined by \( J_1(\lambda_n) = 0 \). This model is plotted for various values of \( b/a \) in Fig. 7-8b,c. In this model, \( a \) is the PCTEM pore radius and \( b \) is half the average PCTEM pore spacing.

The normalization in Fig. 7-8b provides a way to compare flow rates to the one-dimensional diffusion model, \( J = \kappa \Delta c \pi b^2 / L \). Note that the area used in this comparison is \( A = \pi b^2 \) rather than \( \pi a^2 \). As the membrane thickness increases (high \( L/a \)) the one-dimensional model is approached since gas flow spreading within the polymer dominates; entrance resistance to the film imposed by the PCTEM pore array is small compared to the one-dimensional resistance in
the thick film. For thinner films (small $L/a$), the entrance resistance is significant. The gas flow does not spread to access the entire film, resulting in lower flow rates than predicted by the one-dimensional model. The effects of spreading are also reduced for high $b/a$ values, since, for a fixed PCTEM pore size, there is more polymer between pores for gas flow to spread into without cross-talk between pores.

The normalization in Fig. 7-8c emphasizes the small film thickness limit. When the film is very thin, no spreading will occur. In this limit, $J \approx \kappa \Delta c \pi a^2 / L$. Hence, for small $L/a$, it is expected that $J/\kappa a \Delta c \approx \pi (L/a)^{-1}$, independent of $b/a$. This scaling is observed in Fig. 7-8c for $L/a \leq 1$. For larger layer thicknesses, larger $b/a$ results in higher flow rates per support pore, since there is more space for the flow to spread, lowering the resistance. The increase in flow rate (decrease in resistance) from the thin film limit ($J \approx \kappa \Delta c \pi a^2 / L$) predicted for the 200 nm PCTEM ($b/a \approx 3$, $L/a \approx 15$, produced in Section 7.4.2) is a factor of $\sim 7$ (Fig. 7-8c). The support resistance is estimated from the permeance as,

$$ R = \frac{\Delta P}{J} \quad (7-13) $$
7.4.2 Polymer film coating over graphene

The PDMS (Sylgard 184) was mixed with a 10:1 elastomer / curing agent ratio and degassed in vacuum for 1 h. It was mixed at various concentration with heptane filtered through 0.2 μm polytetrafluoroethylene (PTFE) syringe filters. The PCTEM, with or without graphene, was secured to a glass slide with scotch tape on all edges. The membrane was placed in a spin coater and accelerated to 8000 rpm. PDMS solution was pipetted onto the membrane (0.5 mL) and rotation continued for 10 min (Fig. 7-9a). The concentration of PDMS in heptane controls the layer thickness. The membranes were cured for 3 h at 76°C.

The flow rates were measured through PCTEMs without graphene after spin coating with various PDMS concentrations (Fig. 7-9d). Permeance decreases by a factor of ~5,000 as the PDMS concentration is increased from 0-100%. This would allow precise tuning of the support resistance. However, SEM images of the membrane cross section for thick films (e.g., Fig. 7-9f) and light interference observed for thin films indicated that the layer thickness only increased from ~100 nm to 1500 nm when the PDMS concentration increased from 5% to 100%, a factor of only ~20. The support resistance should increase approximately linearly with the film resistance, with deviation resulting from gas spreading in thin films (less than a factor of 7, from Section 7.4.1). The observed reduction in flow rate is not accounted for by polymer layer thickness increases.

Further SEM imaging of the surface of polymer films created with less than 100% PDMS concentrations revealed pin-hole defects in the film (Fig. 7-9i). Any defects in the polymer film will dominate gas transport, resulting in much higher permeance than for a fully intact film. These leakage sources compromise the resistance matching properties of the support membrane. Polymer covered areas will be effectively plugged, and areas where there are defects in the polymer will function as the membrane did without a matched support. As a result, the membranes selectivity
Figure 7-9. PDMS layer coating over graphene on a 200 nm pore PCTEM. a, Direct spin coating method. 
b, Method of PDMS thinning after spin coating. c, PDMS film transfer method. d, Control of support resistance 
with the concentration (w/w) of PDMS in heptane used in spin coating. e-g, Cross section images showing the 
stack, from right to left, of PDMS, graphene, and PCTEM. These images are for a low quality graphene transfer, 
showing areas with graphene coverage (f) and without graphene coverage (g). h, Gas flow rates through 200 nm 
PCTEM with and without graphene, after PDMS spin coating. Flow rates normalized to the value for a bare 
PCTEM without PDMS. i, Pin-hole defects in the PDMS for an estimated 200 nm film thickness. Membranes 
were sputter coated with 80% / 20% Pt / Pd for imaging.
will remain approximately the same, but the permeance will be reduced. Factors that could cause these pin-hole defects include dust particles in the layer during spin coating, solvent evaporation dynamics, or ineffective spreading of a thin layer over PCTEM pores.

Films created with 100% PDMS appeared to be intact. However, the resistance increase of ~50,000 compared to the PCTEM is higher than the estimated ~500 times increase required. Other attempts were made to produce a thin polymer film that was free from defects. One approach was to spin coat 100% PDMS on the membrane, which would be free from defects, then, with the membrane still rotating, add solvent to thin the PDMS film (Fig. 7-9b). Another approach was to spin coat the PDMS on a flat surface and transfer the PCTEM onto the film. A water-soluble polystyrene sulfonic acid (PSS, 5% in water, Sigma-Aldrich) layer was spin coated (2000 rpm, 30 s) on a pre-cleaned glass slide. The PDMS solution was then spin coated over this layer. After curing, the PSS layer was dissolved by placing the glass slide at an angle in a Petri dish and slowly raising the water level, leaving the polymer film floating (Fig. 7-9c). The PCTEM was placed on top of this layer. The assembly was then removed with tweezers and air dried. Both of these methods resulted in pin-hole defects in the thin polymer films.

### 7.4.3 Polymer film coating over multi-layer graphene

Although the resistance of the deposited 1.5 μm thick PDMS film is too high for single-layer membranes (Fig. 7-1), it may be suitable for multi-layer membranes, which have lower tear and intrinsic defect densities, and will likely have a lower selective nanopore density (higher selective nanopore resistance over a support pore).

In multi-layer graphene membranes, the average spacing between aligned intrinsic defects is higher than in single-layer membranes (~10^4 nm for 3 layer compared to ~10^2 nm for single-layer, Fig. 4-5) resulting in higher intrinsic defect resistance. Furthermore, the average spacing
between tears is much higher in multi-layer membranes, since the fraction of pores without graphene coverage decreases exponentially as graphene layers are added. The advantage of this is illustrated in Fig. 7-9h, where measured flow rates through one and three-layer membranes with a PDMS layer are compared to a PCTEM without graphene after PDMS coating. One layer of graphene does not significantly change the gas flow rates, indicating that spreading of gas flow within the polymer from tears or intrinsic defects is significant. However, the flow rate does decrease significantly for a three-layer membrane, indicating that cross-talk between tears or defects is not significant for these membranes.

These results suggest that, while the polymer film resistance is similar to the defect resistance in single-layer graphene, it is lower than the defect resistance in three-layer graphene. Thus, defects will compromise the performance of single-layer graphene membranes with these polymer film supports, but are less important for three-layer graphene membranes.

Multi-layer graphene membranes will also likely have lower created selective nanopore densities than single-layer membranes. While the polymer film resistance is significantly higher than the selective nanopore resistance in single-layer graphene, it will likely be closer to that of multi-layer graphene. Thus, a multi-layer graphene membrane with a polymer resistance layer has the potential to have measurable overall membrane selectivity. However, the higher than necessary support membrane resistance behind the graphene will reduce the overall membrane permeance compared to single-layer graphene on a properly matched support. This idea is pursued with three-layer membranes in Ch. 8.

7.4.4 Polymer film structure

SEM cross-section images of a PCTEM with low graphene coverage (millimeter-scale gaps in graphene coverage) coated with PDMS (Fig. 7-9e-g) reveal an interesting structure of the
polymer on the membrane. In some areas, a 1.5 μm layer is visible on the surface with open PCTEM pores below. In other areas, the PCTEM pores are not visible, suggesting that they have been filled with PDMS. This is also what was observed in PDMS over PCTEMs without graphene, suggesting that those areas of the membrane without visible PCTEM pores were areas without graphene and that polymer is filling PCTEM pores beneath tears in the membrane. This will locally increase the gas flow resistance (~5-10 times) where there would otherwise be high leakage. This is an added benefit of PDMS spin coating to increase the support membrane resistance.

7.4.5 Graphene transfer to a dense, permeable polymer film

The function of the PCTEM in the membrane design using a polymer film for resistance matching is primarily mechanical support. The membrane would operate similarly whether the PDMS layer is on top of the graphene or between the graphene and the PCTEM. In an attempt to improve the graphene coverage, a transfer method resulting in this structure was attempted. PDMS was spin coated on graphene on copper, the PCTEM was stuck to the wet PDMS, the assembly was cured (1.5-8 h), and finally the copper was etched away. This approach was not successful. The resulting graphene transfer showed small (~10 μm) patches of graphene separated by equally

Figure 7-10. Graphene transferred to PDMS on a PCTEM, showing low area coverage of graphene. a,b, Atomic force microscopy (AFM) amplitude and phase. c, SEM image.
large gaps (Fig. 7-10). Possible causes for this poor coverage are polymer contraction during curing; continued curing of the polymer at room temperature after etching; or mismatched thermal expansion coefficients of the polymer, graphene, and copper.

### 7.5 Isotropic pore AAOs

After many failed attempts to find or create a small diameter support membrane with an appropriate gas flow resistance, commercial AAO membranes with uniform pore diameter through the entire cross section became available (Fig. 7-11a-c, InRedox). These membranes have a

![Isotropic pore AAO](image)

**Figure 7-11.** AAO support membrane. **a**, Schematic of isotropic pore membrane cross section. **b**, Illustration of rough AAO surface (reprinted from Ref. 138 with permission from InRedox LLC). **c**, SEM image showing isolated, uniform, 20 nm diameter AAO pores. **d**, SEM image of unpolished AAO. **e**, SEM image of AAO after polishing, showing open pores. **f**, AAO with plugged pores caused by aggressive polishing. A 100 nm diamond particle dislodged from the lapping film is visible on the surface. Membranes in d and e were sputter coated with 80% / 20% Pt / Pd for imaging.
properly matched support resistance (Fig. 7-1, isotropic pore AAO markers) and are available in 20 nm pore diameter, sufficient for intrinsic defect isolation. Note that 20 nm pore membranes were selected because smaller sizes were only available in much smaller thicknesses (e.g., 15 μm for a 10 nm pore membrane instead of 50 μm for a 20 nm pore membrane), not changing the order of magnitude of the support resistance. Another benefit of this structure is that the support pores are perpendicular to the surface, so do not cross (Fig. 7-11c). This prevents cross-talk within the pores, which may occur in PCTEMs, whose pores can have steep angles within the membrane. AAOs are, however, not as amenable to graphene transfer as the PVP-free PCTEMs. These AAOs have surface roughness on the scale of the pore diameter (Fig. 7-11b,d). This structure could leave space between the graphene and AAO for gas transport, resulting in cross-talk between support pores. It could also prevent adhesion of the graphene, such that a suspended layer over the support pores is not obtained. These membranes are also more hydrophilic than the PCTEMs and are damaged by long exposure to the copper etchant, further complicating graphene transfer.

7.5.1 AAO polishing

To promote graphene adhesion and remove the possibility of transport in the space between the graphene and AAO, the AAOs were polished before graphene transfer. The AAO membranes (InRedox) are polished by using a latex gloved finger to rub the membrane over a polishing surface for 90 s (Fig. 7-12a, 7-13a,b). An alumina polishing stone (Spyderco, ultra-fine) with an equivalent 1.2 μm grit size was used for the first cycle, whereas a 100 nm diamond lapping film (Ted Pella) covered in a water film was used for subsequent cycles. This flattens the surface, but removed alumina dust can plug the surface (Fig. 7-11f). The membrane is dipped in sulfuric acid (10%) for 30 s to dissolve the alumina dust and then rinsed in three successive water baths for 30 s. This polishing procedure was repeated for a total of three cycles. SEM images show improved flatness
without plugging the surface pores (Fig. 7-11e). Compared to all the polishing methods attempted, this approach gave the best balance of high percentage membrane area that was well polished and low percentage area with pores plugged on the surface, as observed by SEM.

Gas flow rates were measured through the AAO before and after polishing. The results show that the AAO pores were not plugged by the polishing procedure (Fig. 7-12g).

*Other attempts to polish AAOs*

Other, less successful attempts were made to polish the AAO. These included rubbing two AAOs together, polishing with red rouge and a jewelry buff, floating on an ammonium hydroxide and hydrogen peroxide solution to etch the surface, and using an Allied MultiPrep polishing system

![Diagram of AAO polishing process]

**Figure 7-12.** AAO membrane transfers. a, AAO polishing and direct graphene transfer. b-e, SEM images of graphene on AAO support. f, Photograph of graphene on an AAO support, with O-ring in place for gas flow measurements. g, Comparison of flow rates after polishing and after graphene transfer. Flow rates are normalized by the flow rate through a bare, unpolished AAO.
with a diamond lapping film. These approaches did not provide as uniformly flat a surface without plugging the AAO pores.

Paraffin wax filling of the pores for polishing was attempted to prevent alumina filling the pores, but did not fix the problem. An attempt was made to prevent AAO fracture during polishing by securing it to a flat polishing puck with acetone soluble crystal bond. However, the crystal bond often plugged the support pores even after heating the membrane and soaking in a stirred acetone bath.

### 7.5.2 Graphene transfer to AAO

To transfer graphene onto the polished AAO, graphene on copper is first etched for 5 min by floating on APS to remove backside graphene (Fig. 7-12a, 7-13c-e). After rinsing, the graphene on copper is floated on ammonium persulfate (APS-100, Transene) until the copper has been completely removed. This leaves a square of graphene floating on the etchant. The polished side of the AAO is gently pressed into the graphene against surface tension, using a vacuum TEM grid holder. The AAO is scooped onto a water surface with a glass slide within 30 s of the transfer, since APS etches the AAOs. After rinsing, the membrane is removed and air dried.

SEM images of graphene on AAOs are presented in Fig. 7-12b-e. Gas flow rate measurements show similar graphene coverage to that achieved on PCTEMs (Fig. 7-12g). This
support membrane and single-layer graphene transfer approach gives proper support resistance matching to the estimated selective nanopore resistance (Fig. 7-1), and is pursued further in Ch. 8.

It should be noted that the time scale for AAOs to dissolve in APS is hours to days. A control experiment was performed in which an AAO was floated on APS for 2 min, then rinsed. Gas flow rates were measured before and after, and showed no detectable change, suggesting no significant damage to the AAO in the short exposure time during transfer.

Variations of the graphene transfer to AAOs

The graphene transfers to AAO have a low yield rate. Various methods to improve the robustness of the transfer were attempted, but the “direct” method described above provided the best coverage with the lowest amount of contamination on the graphene.

Poly(methyl methacrylate) (PMMA) and polycarbonate (PC) mediated transfers were both attempted, in which a sacrificial layer of the polymer is spin coated (1% PMMA in anisole or 1% PC in chloroform) on graphene on copper which has had its backside graphene removed. The remaining copper is then etched, leaving graphene with a polymer coating floating on the etchant, which is scooped onto a water surface to rinse. The graphene is later scooped onto an AAO, heated at 60°C on a hot plate for 1 h, before the polymer is dissolved in a solvent (acetone for PMMA, chloroform for PC) for 1 h. The membrane is then exposed to a 5% hydrogen in argon atmosphere at 275°C for 1 h in a tube furnace to remove polymer residue. These transfers had higher yield but the resulting membranes had undesirable polymer contamination.

Similar sacrificial layer methods were attempted using camphor (10% in ethanol, coated with a droplet by syringe) and octadecane (50% in hexane, spin coated). When heated, camphor (50°C) quickly sublimes and octadecane (250°C) melts then evaporates. It was hoped that these layers, not requiring a solvent to remove, would be less strongly bound to the graphene and would
produce lower contamination on the membrane. These methods did not result in graphene suspended over the support pores; gas flow measurements show no change compared to a support membrane without graphene. However, graphene was visible on solid areas of the membrane after the camphor mediated transfer.

Methods to improve the adhesion between the graphene and AAO were also explored. Coating the AAO with platinum / palladium (80%:20%, sputter coating, 2 nm), gold (sputter coating, 2 nm), and nickel (thermal evaporator coated, 3 nm) did not reduce the flow rate through the AAO without graphene, but also did not improve the graphene transfer yield. Silanization of the AAO was also attempted. The membrane was exposed to silane (200 μL) under vacuum for 90 min, vacuum without silane for 90 min, water vapor for 12 h (200 μL), and finally heated at 120°C for 3 h. This procedure was employed with (heptadecafluoro-1,1,2,2-tetra-hydrodecyl) trichlorosilane in an attempt to improve hydrophobicity, and (3-phenylpropyl) trichlorosilane with and without an equal volume of (3,3,3-trifluoropropyl) trichlorosilane to improve adhesion with graphene. The first method resulted in partial plugging of the AAO pores before graphene transfer. The other approach did not, but also did not improve the transfer yield.

7.6 Conclusions

The support membrane structure serves the essential functions of reducing leakage through tears and isolating intrinsic defects in graphene membranes. An optimal support has a gas flow resistance that is well matched to the selective nanopore resistance in graphene and a characteristic length scale smaller than the intrinsic defect spacing. This chapter has focused on the selection or fabrication of a support structure with these characteristics that is also amenable to graphene transfer.
Small diameter commercial supports were tested. Most had a thin active layer with the
desired small pore size, but a much larger pore size in the bulk of the membrane, resulting in lower
resistance than required. Attempts to increase the resistance of the commercial support using
laminate structures or particle filled pores were not successful.

Depositing a dense, permeable polymer film on graphene was shown to allow for resistance
tuning. However, the thinnest films that could be created without pinhole defects were too thick to
isolate tears in single-layer membranes. This approach was shown to be a viable option for
resistance tuning of multi-layer membranes, if lower permeance can be tolerated than is possible
with single-layer graphene on an optimized support. This membrane structure is used in selective
nanopore generation experiments in Ch. 8.

Constant small pore diameter AAO membranes were found to provide close matching of
the support and graphene resistance. The surface roughness of these membranes requires that they
be polished prior to graphene transfer. This type of membrane structure is also used in selective
nanopore generation experiments in Ch. 8.
Chapter 8

Selective nanopore creation

With graphene on a properly matched support membrane, it may be possible to create a selectively permeable membrane by introducing selective nanopores. Three general approaches are taken: (1) pores are introduced by high density ion bombardment, (2) pores are created by dry or wet etching, and (3) pores are first nucleated by low density ion bombardment and then enlarged by etching.

8.1 Ion bombardment

Bombarding graphene with high energy ions can damage the lattice creating single or multi-vacancy defects.\textsuperscript{117,118} In this section, the possibility of using ion bombardment to create gas selective nanopores in macroscopic areas of graphene is explored.

8.1.1 Ion bombardment methodology

Ion bombardment was performed in an FEI Helios Nanolab DualBeam 600 by acquiring 4096$\times$3536 pixel images. Bombardment was performed with gallium ions at a working distance
of 4 mm, 100× magnification, 19 nA current, 8.0 kV voltage (unless otherwise specified), and at
52° to the ion beam (unless otherwise specified).

It was found that ensuring that focused ion beam images did not overlap was not sufficient
to prevent overlap between areas bombarded with ions on the sample, at least at relatively high
bombardment densities. This is shown in Fig. 8-1a, where a bare 200 nm PCTEM is bombarded
at a sufficiently high density that gallium embedded in the PCTEM is visible. The bombardment
pattern shows dark areas of overlap between bombardment windows, even though the produced
images did not overlap.

Overlap between adjacent bombardment sites means that different areas of the membrane
will be bombarded at different densities, since some places will be bombarded multiple times.
Based on measurements of the size of the dark bombarded area in Fig. 8-1a, the distribution of
membrane area bombarded multiple times can be estimated for different bombardment window
 spacings (Fig. 8-1c-g). For example, in the configuration in Fig. 8-1e, a significant fraction of the
area is bombarded six times (Fig. 8-1g). At low bombardment densities, the graphene permeance
due to selective nanopores will be low, and may not be resolved by gas transport measurements.
At high bombardment densities, the graphene may be so damaged that gas transport is non-
selective. If some areas of the membrane are being bombarded at much higher rates than other
areas, the membrane may go from having too low a selective pore permeance to be measured to
having too many damaged areas to measure selective transport, as the bombardment density per
scan window is incremented. It is therefore desirable to only bombard each area once.

From the measured bombardment window size, it was estimated that spacing the windows
by two window widths horizontally and three window heights vertically would provide for no
overlap at 52° bombardment. This was tested on the membrane in Fig. 8-1b, where it is seen that
this spacing prevents overlap between bombardment sites. However, Fig. 8-1b suggests another undesirable feature of the ion bombardment procedure. Along the right edge of each bombardment window is a dark strip. This is likely the result of the ion beam dwelling at the start of each line scan, resulting in higher density bombardment there.

Figure 8-1. Ion bombardment patterns for 52° bombardment. a, Photograph of bombardment window overlap pattern resulting from one-window spacing in x and y for $2 \times 10^{14}$ ion/cm$^2$. b, Photograph of bombardment window overlap pattern for two-window spacing in x and three-window spacing in y, at $4 \times 10^{15}$ ion/cm$^2$ (except in the corners, where lower density was used). c-f, Various bombardment patterns (left) and computed overlap patterns (right). g, Distribution of membrane area scanned multiple times as a result of bombardment window overlap for various bombardment patterns. $L$ is the bombardment window length.
8.1.2 Graphene damage due to ion bombardment

Ion bombardment was first tested on graphene on PCTEMs. Figure 8-2 presents flow rates as a function of ion bombardment density for one-layer graphene on 10 nm pore PCTEMs, chosen for defect isolation, and three-layer graphene on 200 nm PCTEMs, chosen for defect sealing. Neither set of membranes showed increases in selectivity with ion bombardment density. The results show that the flow rates through these membranes increase significantly between $10^{14}$ and $10^{15}$ ion/cm$^2$ bombardment. This indicates that large pores or damaged regions are being created in graphene at these bombardment densities.

8.1.3 Selectivity of bombarded three-layer graphene

One possible reason that selectivity was not observed in graphene on PCTEMs is that the support resistance is not properly matched. Similar experiments were performed on three-layer graphene with a polymer resistance matching layer.

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**Figure 8-2.** Gas flow rates through graphene bombarded at 52° and relatively high densities. a, One-layer graphene on 10 nm PCTEM (bombarded at 8 kV). b, three-layer graphene on 200 nm PCTEM (bombarded at 1 kV, 5 kV, and 16 kV for densities of $\sim 10^{13}$, $\sim 10^{14}$, and $\sim 10^{15}$ ion/cm$^2$, respectively).
Three-layer graphene on 200 nm PCTEMs was bombarded at various densities and then spin coated with PDMS (Fig. 8-3a). Helium and sulfur hexafluoride flow rates were measured through these membranes (Fig. 8-3b,c, uncertainty analysis is discussed in Appendix C). The results show a significant increase in permeance between $10^{14}$ and $10^{15}$ ion/cm$^2$ bombardment, consistent with measurements without PDMS. They also show an increase in selectivity from that of the PDMS (~2) to near the Knudsen selectivity (~6).

**Figure 8-3.** Selective transport through three-layer graphene with a polymer film layer. **a,** Membrane fabrication. **b,** Helium flow rate, normalized by the flow rate through a PCTEM with a PDMS coating and without graphene. Ion bombardment density is the maximum bombardment density of any area of the membrane. **c,** Corresponding He/SF$_6$ selectivity. **d-f,** Illustration of membrane structure for different bombardment densities. The bombardment densities corresponding to c-f are shaded in b,c. Estimated measurement uncertainty indicated in b,c is discussed in Appendix C.
An explanation for the results obtained in Fig. 8-3b,c is provided in Fig. 8-3d-f. At low bombardment densities (~10^{14} ion/cm^2, Fig. 8-3d), the dominant flow path is through PDMS filled tears in the membrane. As a result, the permeance is low (Fig. 8-3b, blue region) and the selectivity is that of the PDMS (Fig. 8-3c, blue region). At moderate bombardment densities (~10^{15} ion/cm^2, Fig. 8-3e), the graphene permeance becomes significant compared to that through tears. Membrane flow rate increases (Fig. 8-3b, green region) as does selectivity (Fig. 8-3c, green region). At high bombardment densities (>2 \times 10^{15} ion/cm^2, Fig. 8-3e), the graphene is destroyed. The support pores fill with PDMS during spin coating resulting in a drop in flow rates (Fig. 8-3b, red region) and the selectivity returning to the value for PDMS (Fig. 8-3c, red region).

An important feature of these results is that, even at the optimal bombardment density, the selectivity does not exceed the Knudsen selectivity (Fig. 8-3b,c). This suggests that, by the bombardment density where the graphene is sufficiently permeable to influence overall membrane flow rates, the pores in graphene are larger than the diameter of gas molecules. This is consistent with the damage observed in three-layer graphene without PDMS at this bombardment density (~10^{15} ion/cm^2, Fig. 8-2b). Selectivity is likely resulting from differences in molecule mass (Fig. 1-1, Knudsen regime) rather than molecule size (Fig. 1-1, molecular sieving regime).

Raising membrane selectivity beyond the Knudsen selectivity will require methods to produce high graphene permeance from smaller nanopores. Creating a high density of smaller pores without damaging the graphene will likely be simpler in single-layer graphene. Furthermore, methods that enlarge nucleated pores by etching may result in permeable nanopores with less damaged graphene. These approaches are explored in the remainder of this chapter.
8.2 Potassium permanganate etching

O’Hern et al.\textsuperscript{84} demonstrated sub-nanometer pore generation in graphene by low density ion bombardment followed by acidic potassium permanganate (KMnO\textsubscript{4}) etching. Ion bombardment creates defect sites in graphene, which are more susceptible to etching. These defect sites are then enlarged by permanganate ion oxidation.\textsuperscript{84,119}

O’Hern et al.\textsuperscript{84} performed high resolution STEM imaging of the pores generated by this procedure (Fig. 2-9h-j). A significant portion of the pore size distribution is less than 0.55 nm, the kinetic diameter of SF\textsubscript{6}, and may be suitable for gas separation experiments.

8.2.1 Estimated nanopore selectivity by KMnO\textsubscript{4} etching

From pore size distributions obtained for different bombardment and etching conditions,\textsuperscript{84} the permeance and selectivity of graphene was estimated. The permeance of each gas is estimated from the equation for ideal gas effusion through a small orifice, and the ratio taken to obtain selectivity. The pressure normalized gas flux, $J$ [mol/s-Pa], is estimated as,

$$J = \frac{\bar{A}_S \rho_S}{\sqrt{2\pi MRT}}$$  \hspace{1cm} (8-1)

where $\rho_S$ is the pore density and $\bar{A}_S$ is the average area of generated pores, estimated by,

$$\bar{A}_S = \sum_{d_i > D_m} \frac{\pi}{4} (d_i - D_m)^2 / \sum_{d_i} 1$$  \hspace{1cm} (8-2)

where $d_i$ is the diameter of pore $i$, and $D_m$ is the kinetic diameter of the molecule. That is, the finite size of the gas molecule is accounted for in estimating the effective pore area available for transport. The pore density was similarly estimated from these images ($\sim 10^{12}$ cm\textsuperscript{-2}), and used to estimate total graphene permeance.\textsuperscript{84}
Figure 8-4. Predicted graphene permeance and selectivity created by ion bombardment followed by potassium permanganate etching. The legend shows ion bombardment conditions. Predictions are based on the pore size distribution and density obtained from STEM images.\textsuperscript{84} a, Permeance. b, Selectivity.

It should be noted that flow rate reductions due to steric hindrance through pores with similar size to the gas molecules (Section 2.3.1) have not been included in this estimate. The reason for this is that molecular simulations suggest that for many types of gases, that reduction is compensated for by an increase in permeance due to an adsorption pathway.\textsuperscript{70} Furthermore, these estimates are for the graphene only. Changes in permeance and selectivity due to tears, intrinsic defects, and the support membrane are not included in this calculation.

Figure 8-4 presents the predicted gas permeance and selectivity of graphene created by this approach. Selectivities of up to ~100 are predicted for He/SF\textsubscript{6}. These are estimates of the maximum selectivity attainable by this selective pore generation method, if leakage sources in the membrane are adequately addressed without significantly increasing the resistance to flow in the support compared to graphene.
8.2.2 Methodology for pore creation by KMnO₄ etching

Graphene membranes were bombarded as described in Section 8.1.1. The membranes were floated, graphene-side-down, on 1.875 mM KMnO₄ in 6.25% sulfuric acid. Membranes were then rinsed in water and soaked in ethanol before drying.

8.2.3 Gas permeance measurements on KMnO₄ etched membranes

Gas flow rates and selectivity for low defect density graphene (produced in lab on cold rolled copper foil) on 200 nm PCTEMs are presented in Fig. 8-5. Interfacial polymerization was performed on these membranes prior to ion bombardment for leakage sealing.

A very slight increase (from ~5 to ~5.4) in selectivity is observed for early etch times (~20 min) with a corresponding increase in permeance. However, selectivity drops as etch time increases further. The rise in both helium and sulfur hexafluoride flow rates at early times without

![Figure 8-5. Change in gas permeance due to potassium permanganate etching. The data are for one membrane etched for many increments of time. The membrane is one-layer graphene on a 200 nm PCTEM after interfacial polymerization and 2×10¹³ ion/cm² bombardment. a, Flow rate. b, Selectivity.](image)
creating the high selectivity predicted in Fig. 8-4, suggests that the etching process is also opening leakage pathways through the graphene.

Although not conclusive evidence, these results suggest that, while it is possible that potassium permanganate etching is creating gas selective nanopores in graphene, even with interfacial polymerization to seal the membrane, leakage sources are providing higher permeance than selective nanopores. Repeating this pore generation procedure on a graphene membrane with a properly matched support resistance may fix this problem. However, the matched AAO support membranes are incompatible with this etchant. As a result, the single-layer resistance matched membranes cannot be used directly with this pore generation method. It is possible that modifications to the pore generation procedure, using a compatible acid or generating pores by a similar method before transferring graphene onto the AAO, could solve this issue. This was not pursued.

8.3 UV ozone etching

Selective nanopores have been created in small areas of graphene by etching in a UV ozone cleaner. The sample is exposed to UV light at ambient conditions. This energy converts oxygen in the air into ozone and reactive atomic oxygen and can also break bonds in the sample, creating pores. UV ozone exposure is capable of generating pores in graphene without nucleation by ion bombardment, though, a more uniform pore size distribution can be obtained after bombardment.

Graphene membranes were placed in a UV ozone cleaner (BioForce Nanosciences UV/Ozone ProCleaner, 185 Hz) for various lengths of time. Single-layer graphene on 10 nm and 200 nm pore PCTEMs as well as three-layer graphene on a 200 nm pore PCTEM were tested.
While the gas permeance increases with exposure time (Fig. 8-6), no change in membrane selectivity was observed.

These measurements were performed before a matched support membrane was available. Shorter exposure times on resistance matched membranes have the potential to show increases in selectivity. Furthermore, ion bombardment prior to etching may improve pore size uniformity and increase membrane selectivity. This is attempted with a more aggressive oxygen plasma etching process in the next section.

### 8.4 Oxygen plasma etching

Similar to UV ozone etching, oxygen plasma etching can create or enlarge defects in graphene through exposure to UV, which can break graphene bonds, in an environment of reactive oxygen species.\textsuperscript{82,124}
8.4.1 Pore creation and enlargement by oxygen plasma etching

As an initial feasibility test for using oxygen plasma etching to generate pores, graphene on a 200 nm pore PCTEM was exposed to oxygen plasma (Harrick Plasma Expanded Plasma Cleaner PDC-001, Maximum 30 W power, low power setting, 600 mTorr) with and without ion bombardment (as described in Section 8.1.1). Gas flow rates (Fig. 8-7) were not observed to increase until ~35 s of exposure, indicating that the etching process is sufficiently slow to permit use of this method. Furthermore, these measurements indicate that graphene is completely destroyed by the etching process after ~90 s.

These observations are confirmed by SEM images of oxygen plasma etched membranes (Fig. 8-8). On the unbombarded membrane, after 30 s of etching, no created pores are visible in the SEM images (Fig. 8-8a,b). By 45 s, several larger (~50 nm) pores are visible over the membrane (Fig. 8-8c-e) explaining the large rise in flow rate (Fig. 8-7). After 60 s of etching, the

![Figure 8-7. Graphene damage due to O₂ plasma exposure. Graphene is on 200 nm pore PCTEMs. Each data point represents a different membrane. One set of membranes was bombarded while the other was not. Graphenea graphene was used in these experiments.](image)
graphene over most of the PCTEM is gone (Fig. 8-8f,g), consistent with the observed increase in gas flow rate to the value of a PCTEM without graphene (Fig. 8-7).

Similar features are observed on the membrane that was bombarded with ions before oxygen plasma etching (Fig. 8-8h-m). However, in the bombarded membrane, at 45 s of etching, a much higher density of smaller pores (~20 nm) is observed (Fig. 8-8j-m) than on the unbombarded membrane. Although the created pores visible in these SEM images are far too large for molecular sieving, the images suggest that they have grown from much smaller pores through plasma etching. Smaller, potentially selective pores, likely exist at shorter plasma exposure times. Furthermore, these results suggest that ion bombardment has successfully increased the nanopore density after plasma etching.

8.4.2 Estimated nanopore selectivity by oxygen plasma etching

Pore size distributions created by ion bombardment followed by oxygen plasma etching were obtained through STEM imaging (by Doojoon Jang) similar to that performed for intrinsic defects\textsuperscript{35} and pores created by potassium permanganate etching.\textsuperscript{84} An example pore size distribution is plotted in Fig. 8-16c (courtesy of Doojoon Jang (MIT) and Juan-Carlos Idrobo (ORNL)).

The permeance and selectivity of graphene areas with these pore size distributions were estimated with Eq. 8-1 (Fig. 8-9). Maximum selectivity of ~35 is predicted for this pore size distribution. Consistent with gas flow measurements on PCTEMs (Section 8.4.1), selectivity decreases by ~30 s of exposure. For the graphene sample treated while on a PCTEM, the lower permeance at 75 s etch time compared to 50 s etch time (Fig. 8-9a) may result from factors such as variability in the pore creation procedure, error introduced by limitations on the total area of the
Figure 8-8. SEM images of O$_2$ plasma etched membranes for which flow rates are plotted in Fig. 8-7. 
a.b, Unbombarded, 30 s etch.  
c-e, Unbombarded, 45 s etch.  
f.g, Unbombarded, 60 s etch.  
h,i, Bombarded, 45 s etch.  
j-m, Bombarded, 60 s etch.  
Graphenea graphene was used in these experiments.
sample that can be imaged in a reasonable time, or differences in the level of contamination covering pores on the sample.

### 8.4.3 Performance of sealed graphene membranes

In an effort to improve on the membrane performance measured in Section 8.4.1, similar oxygen plasma pore generation experiments were performed on lower leakage membranes. Lower intrinsic defect density graphene (produced in lab on cold rolled copper foil) was transferred onto 200 nm PCTEMs, and were then sealed by interfacial polymerization.

Measured flow rates and selectivities are presented in Fig. 8-10. Selectivity increases slightly at early etch times before gradually decreasing to the value of the bare PCTEM as graphene is destroyed. A selectivity peak is obtained with this higher quality graphene even without polymer sealing, although higher selectivities are achieved on the sealed membranes. These results suggest that gas selective pores have been generated by oxygen plasma exposure. However, selectivity has
Figure 8-10. Permeance and selectivity for O₂ plasma etched membranes. Each series of data points was measured on one membrane. Interfacial polymerization was performed on two of the membranes. Ion bombardments was done at 52° incidence and 2×10^{13} ion/cm². Low defect density graphene (produced in lab on cold rolled copper foil) was used in these experiments.

not increased beyond the Knudsen selectivity (~6), so it is not clear how the size of the pores created with measureable permeance compare to the gas molecule diameters.

It should be noted that these experiments were conducted several months after those of Section 8.4.1. The longer etch times required to remove graphene from the membrane in Fig. 8-10 reflect process variation.

**8.4.4 Selectivity of plasma etched graphene on AAOs**

The permeance and selectivity of created nanopores can be better tested on resistance matched support membranes. Using single-layer graphene on AAOs (Section 7.5), the selective pore resistance is expected to be similar to the support membrane resistance. As a result, measurements will be more sensitive to the permeance of selective nanopores and the overall membrane is more likely to exhibit gas selectivity.
Table 8-1. Summary of graphene on AAO membranes that were measured. Ion bombardment was performed at 52° from vertical.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Graphene coverage</th>
<th>Bombardment density [ion/cm²]</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support Polished AAO without graphene</td>
<td>0%</td>
<td>0</td>
<td>Control measurements</td>
</tr>
<tr>
<td>Membrane 1 Graphene on polished AAO</td>
<td>88%</td>
<td>$2 \times 10^{13}$</td>
<td>Short increment etch time sweep</td>
</tr>
<tr>
<td>Membrane 2 Graphene on polished AAO</td>
<td>73%</td>
<td>$2 \times 10^{13}$</td>
<td>Flow rates of various gases</td>
</tr>
<tr>
<td>Membrane 3 Graphene on polished AAO</td>
<td>73%</td>
<td>$2 \times 10^{13}$</td>
<td>Small number of etch times</td>
</tr>
<tr>
<td>Membrane 4 Graphene on polished AAO</td>
<td>72%</td>
<td>$6 \times 10^{13}$</td>
<td>Small number of etch times</td>
</tr>
</tbody>
</table>

Graphene was transferred to polished 20 nm pore, isotropic AAOs by the method described in Section 7.5.1-2. The membrane was bombarded with ions by the method described in Section 8.1.1 and then exposed to oxygen plasma as described in Section 8.4.1 (Fig. 8-11). Four membranes were measured, as summarized in Table 8-1.

*He / SF6 selectivity by oxygen plasma etching*

Oxygen plasma etching increases the gas permeance of the membrane (Fig. 8-12a). At long etch times (~5 min), the graphene is sufficiently destroyed that the flow rates increase to near the value for the AAO prior to graphene transfer (Fig. 8-12a, Membrane 1). At etch times $\leq 100$ s, the helium flow rate increases faster than the sulfur hexafluoride flow rate. This results in a He/SF$_6$ flow rate ratio exceeding the Knudsen effusion limit (Fig. 8-12b), providing evidence of molecular sieving based selective gas transport through the graphene. That is, a significant portion of the gas transport is likely to be through pores with size similar to that of the gas molecules. The highest membrane selectivity attained is 8.4, compared to the Knudsen effusion limit of 6.0. At longer etch times, the selectivity drops, returning to the value of the bare AAO membrane once the pores in the graphene become sufficiently large (Fig. 8-12b, inset).

![Figure 8-11. Selective pore creation process for graphene on AAO.](image-url)
A significant portion of the flow through these membranes is leakage through open AAO pores. To further investigate the properties of the porous graphene, a model was developed to extract the gas permeance and selectivity of the graphene areas from measurements of the overall membrane. This was done with the assumed resistance model inset in Fig. 8-12c; gas transport can occur through graphene over the AAO pores or through open AAO pores. The permeance of the
AAO without graphene, $J_i^{(0)}$, for gas species $i$, was measured prior to graphene transfer for each membrane. Permeance was also measured after transfer, $J_i^{(1)}$, and used to estimate the graphene coverage as,

$$
\gamma = 1 - \frac{J_i^{(1)}}{J_i^{(0)}_{SF_6}} 
$$

(8-3)

Note that, because the AAO pore diameter is so small, most intrinsic defects will result in a graphene resistance over the AAO pore that is negligible compared to that of the support. Thus, the contribution of intrinsic defects are largely included in this estimated coverage. The resistance of the graphene is then,

$$
\left( \frac{R_s}{R_{AAO}} \right)_i = \left[ \left( \frac{J_i^{(1)^{t^i}}}{J_i^{(1)}} - 1 \right) \left( \frac{1 - \gamma}{\gamma} \right) \right]^{-1} - 1
$$

(8-4)

where $J_i^{(1)^{t^i}}(t)$ is the measured permeance of the membrane with graphene after ion bombardment and etching for time $t$. From this, the graphene permeance, $j_i$, to species $i$ is calculated as,

$$
j_i = \frac{1}{\left( \frac{R_s}{R_{AAO}} \right)_i} \left( \frac{1}{R_{AAO}} \right) \left( \frac{1}{\pi D_{AAO}^2} \right)
$$

(8-5)

The ratio of graphene permeances to different gas species gives the graphene selectivity for that gas pair. Extracted graphene permeances and selectivities are presented in Fig. 8-12c,d. While overall membrane selectivities do not exceed 8.4, graphene selectivities are estimated to be as high as 22 (Fig. 8-12d). Suitable leakage sealing methods would be required for the overall membrane permeance to approach this value with the current support structure and selective pore size distribution. Differences in maximum selectivity and the etch time at which this occurs may be due to a sensitivity of the created pore size distribution to small changes in conditions during bombardment and etching.
Selectivity to different gases

Flow rate measurements were performed for the gases listed in Table 8-2. The resulting membrane selectivities to helium over each gas are shown in Fig. 8-13a,b. This value is normalized by the corresponding Knudsen selectivity in Fig. 8-13c,d. These data are plotted both with respect to gas molecule kinetic diameter (Fig. 8-13a,c) and molecular weight (Fig. 8-13b,d).

The Knudsen selectivity of gas A over gas B is $\sqrt{\frac{M_B}{M_A}}$. Figure 8-13b shows that this membrane has selectivities slightly exceeding this limit. This increase is seen more clearly by normalizing by the Knudsen selectivity (Fig. 8-13c,d), which shows that for this membrane the He / SF$_6$ selectivity is approximately 35% above the Knudsen selectivity.

Normalized selectivity appears to be more strongly correlated with molecule size than molecular weight (Fig. 8-13c,d), providing further evidence of size based transport. This is seen for Ar, O$_2$, N$_2$, and CH$_4$, which have increasing kinetic diameter in this order and decreasing molecular weight (Table 8-2); the normalized helium selectivity to these gases increases with kinetic diameter (Fig. 8-13) but decreases with molecular weight (Fig. 8-13d). However, these differences are within experimental uncertainty. This may be the reason that CO$_2$ does not follow this trend. Another possibility is that the quadrupole moment of CO$_2$ causes it to interact strongly

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molecular weight, $M_i$ [g/mol]</th>
<th>Kinetic diameter, $d_i$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.00</td>
<td>2.6</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2.02</td>
<td>2.89</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>44.01</td>
<td>3.3</td>
</tr>
<tr>
<td>Ar</td>
<td>39.95</td>
<td>3.4</td>
</tr>
<tr>
<td>O$_2$</td>
<td>32.00</td>
<td>3.46</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28.01</td>
<td>3.64</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>16.04</td>
<td>3.8</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>146.06</td>
<td>5.5</td>
</tr>
</tbody>
</table>
with functional groups on the graphene or at the pore rim, as observed in simulations of gas transport through graphene nanopores, experiments on single graphene nanopores, and in CO$_2$ selective transport in graphene oxide membranes.

Figure 8-13. Overall membrane selectivity to various gases. a,b, Selectivity to helium over various gases, plotted against kinetic diameter and Knudsen selectivity (proportional to the square-root of molecular weight). c,d, Selectivity normalized by the corresponding Knudsen selectivity, plotted against kinetic diameter and Knudsen selectivity.
The same trends are observed for extracted graphene selectivities (Fig. 8-14). The increase in selectivity over the Knudsen selectivity is more prominent for the graphene than the overall membrane, with extracted graphene selectivities up to three times higher than the Knudsen value.

Figure 8-14. Extracted graphene selectivity to various gases. a,b, Selectivity to helium over various gases, plotted against kinetic diameter and Knudsen selectivity (proportional to the square-root of molecular weight). c,d, Selectivity normalized by the corresponding Knudsen selectivity, plotted against kinetic diameter and Knudsen selectivity.
Additional control experiments

Additional control experiments were performed to further validate the results and modeling assumptions. Gas flow rate measurements were performed over a range of applied pressure differences on a polished AAO membrane without graphene and a bombarded membrane with graphene after 60 s oxygen plasma exposure. Various upstream pressures up to 2 bar were applied with vacuum downstream. The resulting flow rates are nearly linear with pressure (Fig. 8-15a), validating the assumption that $R_{AAO}$ is independent of pressure. That is, it is the same for open support pores and for support pores beneath graphene, which are at a much lower pressure due to the pressure drop across the graphene. The resulting selectivities are also within the experimental error (Fig. 8-15b). Note that the measurement error increases with decreasing pressure difference, because the error in setting the pressure is fixed by the resolution of the gauge while the magnitude of the pressure setting gets smaller.

The contribution of measurement system leakage was quantified by measuring helium and sulfur hexafluoride flow rates with a non-porous polycarbonate film used in place of the

Figure 8-15. Additional control experiment results for AAO membranes. a, Membrane permeance and b, He/SF₆ selectivity measured for different upstream pressures up to 2 bar, with vacuum downstream. c, Decline in flow rate with multiple measurements. Measurement index is the number of times that helium flow rate was measured on the sample. The flow rate of another gas was measured between each helium flow rate measurement. The inset compares the flow rate magnitude to the measurement system leakage. Leakage was measured using a non-porous polycarbonate film in place of a membrane.
membrane. The resulting leakage is orders of magnitude below the flow rates through graphene on the AAO support (Fig. 8-15c, inset).

The flow rates through graphene on AAO membranes after bombardment and etching were found to decrease gradually with volume throughput (Fig. 8-15c). This effect was not observed for a polished AAO membrane without graphene (Fig. 8-12a, Support). This reduction may be a result of contamination plugging created pores during measurement. To compensate for this drift effect in Fig. 8-13,8-14,8-16 helium flow rate was measured between measurements of all other gases. Reported selectivities were always based on the helium measurement taken after the other gas. Using helium flow rates taken after the measurement of the less permeable species ensures that the flow rate reduction will lower the measured selectivity, so as to not over report this value.

Model for graphene membrane selectivity

To gain a better understanding of the experimental results and guide future graphene membrane development, a model was developed to explain the measured membrane permeance and selectivity in Fig. 8-13. As done in extracting graphene permeance, the model includes flow paths through the graphene and underlying AAO pore, as well as through gaps in the graphene coverage (Fig. 8-16). Again, because the AAO pore diameter is so small and the resistance is so high, defects as small as a few nanometers will have negligible resistance compared to the supporting AAO pore, and that support pore will behave as if it is completely open to gas flow.

This model assumes that the graphene permeance due to selective pores can be approximated by an average value, neglecting that there is a finite number of selective pores per AAO pore. This assumption is valid as long as, on average, the graphene over each AAO pore has multiple selective pores. The measured pore size distribution in Fig. 8-16d, for example, has on average 12.5 nanopores larger than 2.6 Å per AAO pore. In model calculations, the value for
graphene coverage ($\gamma$) is not taken from measurements before ion bombardment. Pores a few nanometers in size could be created during etching, whether from ion bombardment sites, small intrinsic defects, or plasma induced nucleation, or tears may be formed during membrane handling or repeated clamping in the measurement setup. The AAO pores with these defects over them will

Figure 8-16. Model for gas permeance and selectivity of graphene on AAO membranes. a, Equivalent resistance model accounting for gaps in graphene coverage ($\gamma$ is the fraction of AAO pores covered in graphene), the resistance of the AAO support, $R_{AAO}$, and the resistance of selective pores in graphene, $R_s$. b, The pore area available for gas transport is estimated from the effective diameter, $D - d$, where $D$ is the pore diameter and $d$ is the gas molecule diameter. c, Example generic log-normal pore size distribution specified by a mean ($\mu$) and standard deviation ($\sigma$). d, Example pore size distribution measured on a TEM grid after vertical ion bombardment at $7 \times 10^{13}$ ion/cm² at 1 kV followed by a 30 s oxygen plasma etch (courtesy of Doojoon Jang). The distribution is normalized such that $\int_{d_{HE}}^{\infty} \bar{P}(D)dD = 1$. e, Measured overall membrane flow rate normalized to the flow rate of that gas through the AAO before graphene transfer, with model fit shown. To compensate for membrane fouling over the course of several measurements, which causes a slow decline in helium flow rate, helium flow rates were measured after measuring each other gas. Selectivity of helium to each other gas was calculated using the helium flow rate measured immediately following the other gas. For each gas other than helium, the data in this panel were computed as the ratio of the first helium flow rate measurement on this sample after 95 s O₂ plasma, divided by the measured selectivity of helium to that other gas. f, Overall membrane selectivity to helium over other gases, normalized to the corresponding Knudsen selectivity, and compared to model predictions. In the d,e insets, the contribution of selective pores in graphene (model, selective) and the large molecule limit due to leakage (model, leakage) are plotted separately.
act as if there is no graphene over them, resulting in an effectively lower graphene coverage. This is accounted for by leaving $\gamma$ as a fitting parameter in the model.

The equivalent resistance, $R$, of the network in Fig. 8-16a can be expressed as,

$$\left( \frac{R}{R_{\text{AAO}}} \right) = \frac{1 + \left( \frac{R_s}{R_{\text{AAO}}} \right)}{1 + (1 - \gamma) \left( \frac{R_s}{R_{\text{AAO}}} \right)}$$

(8-6)

where the average flow rate per AAO pore is given by $J_i = \Delta P/R_i$.

The pore size distribution was modeled as being log-normal (Fig. 8-16c). Skewed probability distributions, representing a variable that cannot be negative, such as pore diameter, and with standard deviation not much less than the mean, are often well fit by a log-normal model. Furthermore, this model distribution captures the general shape of measured created pore size distributions obtained by potassium permanganate etching and oxygen plasma etching (Fig. 8-16d, Ref. 84). However, the measured pore size distributions have a mean pore size smaller than the kinetic diameter of helium (2.6 Å), the smallest gas. Consequently, only pores in the tail of this distribution are permeable to gases. Thus, fitting the permeance model to gas flow measurements with an assumed log-normal pore size distribution will not give information about the complete shape of the pore size distribution, only about the permeable tail; the mean pore size, standard deviation, and size distribution below 2.6 Å obtained by fitting are not meaningful. The gas permeance model is developed for a full log-normal pore size distribution rather than just the tail so that it can be applied to more general pore size distributions for predictive purposes. The general log-normal distribution has the form,

$$P(D) = \frac{1}{\chi D \sqrt{2\pi}} e^{-\frac{(\ln D - \psi)^2}{2\chi^2}}$$

(8-7)

where $\psi$ and $\chi$ are the mean and standard deviation of the random variable $\ln D$, respectively. They
can be obtained from the mean ($\mu$) and standard deviation ($\sigma$) of the distribution by,

$$
\chi = \sqrt{\ln \left( \frac{\sigma^2}{\mu^2} + 1 \right)}
$$
(8-8)

$$
\psi = \ln \frac{\mu}{\sqrt{\sigma^2/\mu^2} + 1}
$$
(8-9)

Note that this distribution is normalized, such that, $\int_0^\infty P(D)dD = 1$.

The gas permeance resulting from this distribution is estimated from the equation for ideal gas effusion (Box 1-1). The effective pore diameter available to gas transport is approximated as $D - d_i$, where $D$ is the pore diameter and $d_i$ is the kinetic diameter of the gas molecule (Fig. 8-16b). Then, the average flow rate [mol/s] of gas $i$ per AAO pore is,

$$
(J_s)_i = \rho_s \frac{\pi}{4} D_{AAO}^2 \frac{\Delta P}{\sqrt{2\pi M_i RT}} \int_0^\infty \frac{\pi}{4} (D - d_i)^2 P(D)dD
$$
(8-10)

$$
= \rho_s \frac{\pi}{4} D_{AAO}^2 \frac{\Delta P}{\sqrt{2\pi M_i RT}} \left[ -2d_i e^{\frac{1}{2}\chi^2 + \psi} \left( 1 + \text{erf} \frac{\chi^2 + M - \ln d_i}{\chi\sqrt{2}} \right) 
+ d^2 \left( 1 + \text{erf} \frac{\psi - \ln d_i}{\chi\sqrt{2}} \right) + e^{2\chi^2 + 2\psi} \left( 1 + \text{erf} \frac{2\chi^2 + M - \ln d_i}{\chi\sqrt{2}} \right) \right]
$$

where $(R_s)_i = \Delta P / (J_s)_i$. Equations 8-5 and 8-9 can be used to calculate membrane permeance and selectivity for values of graphene coverage ($\gamma$), selective pore density ($\rho_s$), and selective pore distribution parameters $\psi$ and $\chi$ (or equivalently, $\mu$ and $\sigma$).

A model fit to the experimental measurements gives $\mu = 0.0273$ Å, $\sigma = 0.0303$ Å, $\rho_s = 1.64 \times 10^{24}$ m$^{-2}$ and $\gamma = 0.684$. The resulting model fit agrees well with measurements (Fig. 8-16e,f). The pore size probability density function, $P(D)$, and selective pore density, $\rho_s$, used in the permeance model are for all pores in the log-normal distribution. However, only pores with
diameter larger than $d_{He} = 2.6 \text{ Å}$ are gas permeable. It is more physically meaningful to consider only pores larger than this diameter, giving a renormalized pore size distribution of,

$$\bar{P}(D) = \frac{P(D)}{\int_{d_{He}}^{\infty} P(D) dD}$$  \hspace{1cm} (8-11)

and a density of gas permeable selective pores of,

$$\bar{\rho}_s = \rho_s \frac{\int_{d_{He}}^{\infty} P(D) dD}{\int_{0}^{\infty} P(D) dD} = \frac{\rho_s}{2} \left[ 1 + \text{erf} \frac{\psi - \ln d_{He}}{\chi \sqrt{2}} \right]$$  \hspace{1cm} (8-12)

Note that $P(D)$ and $\rho_s$ are still used in the model calculations, but from them, $\bar{P}(D)$ and $\bar{\rho}_s$ can be computed. For the model fit in Fig. 8-16, Eq. 8-12 gives $\bar{\rho}_s = 2.6 \times 10^{16} \text{ m}^{-2}$. This is in reasonable agreement with the density of pores with $D \geq d_{He}$ measured from STEM images for the distribution in Fig. 8-16c of $4.0 \times 10^{16} \text{ m}^{-2}$, further corroborating the modeling.

The model fit predicts a graphene coverage of 68%, within the measurement uncertainty of the coverage of 73% measured before bombardment (Table 8-1). The lower coverage obtained by the model fit may also reflect nanometer-scale pores opening or graphene damage sustained during membrane handling.

The model further reveals the significant effect of leakage on the qualitative trends in measured selectivity. The inset plots in Fig. 8-16e,f separate the contributions of leakage flow from selective flow through graphene. Without leakage, the normalized flow rates decrease and normalized selectivities increase rapidly for larger molecule diameters (blue curves), as a greater portion of the pore size distribution is below that molecule size. However, the normalized flow rates and selectivities show saturation behavior at larger diameters due to leakage (red curves), which dominates transport of larger molecules, imposing an upper bound on normalized
selectivities. The concave-down trend in measured normalized selectivities (Fig. 8-16f) is a further illustration of the significant effect that leakage has on graphene membrane performance.

**Graphene membrane performance**

The extracted graphene permeances and selectivities for He/SF$_6$, H$_2$/CH$_4$, and H$_2$/CO$_2$ are compared to the graphene membranes created by Koenig et al.$^{33}$ and Celebi et al.$^{12}$ in Fig. 8-17. The results are also compared to estimated selectivity and permeance from created selective pore size distributions from STEM images.

Koenig et al.$^{33}$ measured gas permeance through a single or a few sub-nanometer pores. The CH$_4$ and SF$_6$ flow rates they measured were orders of magnitude lower than for smaller gases, giving high selectivities. This is made possible by having a single pore size in the appropriate size range for molecular sieving. However, the actual membrane permeance is relatively low for ~1 nanopore in a micron-scale area of graphene.

Celebi et al.$^{12}$ used helium ion milling to create an array of $10^3$-$10^6$, ~7.6 nm pores. The 4% membrane porosity gave a very high graphene permeance. However, due to the relatively large size of these pores, the selectivity does not exceed the Knudsen effusion limit.

The centimeter-scale membranes measured here have ~$10^{12}$-$10^{13}$ pores, representing a significant advancement in the size of graphene membranes with measured selectivity. The graphene selectivities measured on these membranes exceed the Knudsen limit, indicating that a significant portion of the gas flow is passing through sub-nanometer pores. However, this increased selectivity comes at the expense of permeance (Fig. 8-17). The graphene permeance measured here is larger than that obtained by Koenig et al.$^{33}$ because the selective pore density is higher, but lower than that obtained by Celebi et al.$^{12}$ because the porosity is lower. Similarly, the selectivity measured here exceeds the Knudsen limit, indicating that the selective pore sizes are
smaller than those produced by Celebi et al., but the width of the pore size distribution produces significantly lower selectivities than achieved by Koenig et al.33

The measured graphene selectivities are in reasonable agreement with those predicted for measured pore size distributions (Fig. 8-17). However, the permeance is approximately an order of magnitude lower than predicted at these selectivities. Some of this difference may be due to an

Figure 8-17. Extracted graphene selectivity and permeance compared to those of previous experiments and estimated from measured pore size distributions. a, He/SF6, b, H2/CH4, c, H2/CO2. The data from Koenig et al.33 in (a) approximate the He permeance as the value for H2, since He measurements were not reported. Koenig et al.33 mention flow rate measurements for SF6 but do not present them, so the He/SF6 selectivity was approximated as the measured H2/CH4 selectivity. Celebi et al.12 do not directly present He/SF6 or H2/CH4 selectivities. Based on the discussion in their paper, the plotted values are approximated as the Knudsen selectivities for those gases. Robeson polymer upper bounds are from Ref. 4.
overestimate of the pore density from STEM images; acquired images tend to be of interesting features, such as pores, rather than pristine areas, potentially biasing the estimate. Contamination covering some pores during measurement could also contribute to lower permeance. Furthermore, the permeance calculated from STEM images uses a simplified transport model that could introduce significant error in the estimates.

Robeson limits are available for $\text{H}_2/\text{CH}_4$ and $\text{H}_2/\text{CO}_2$ membranes. The measured graphene performance is compared to these limits in Fig. 8-17b,c. For $\text{H}_2/\text{CH}_4$, the graphene performance is

![Figure 8-18](image-url)

**Figure 8-18.** Comparison of measured graphene performance with simulation predictions for a, $\text{H}_2/\text{CH}_4$, and b, $\text{H}_2/\text{CO}_2$. The permeance data of Koenig et al. are scaled to have a pore density of $10^{12}$ pores/cm$^2$, assuming that a single pore was measured in their experiments. The permeance data of Celebi et al. are the values actually measured on graphene, without scaling by an assumed pore density. The $\text{H}_2/\text{CH}_4$ selectivity of Celebi et al. is assumed to be the Knudsen selectivity based on the discussion in that work, since it is not directly reported. Robeson polymer upper bounds are from Ref. 4 and assume a 100 nm active layer thickness. For simulation data, a pore density of $10^{12}$ cm$^{-2}$ is assumed to calculate permeance, unless the material is inherently porous. In that case, the actual material porosity is used. The scaling model from Section 2.3 is also plotted, using parameters for $\text{H}_2/\text{CH}_4$ and $\text{H}_2/\text{CO}_2$ in a and b, respectively.
just below the Robeson limit, making it competitive with state of the art polymer membranes with selectivity just above the Knudsen ratio. For H₂/CO₂, the graphene performance is above the Robeson limit. However, it should be noted that these values are extracted for just the areas of the membrane with graphene; they represent a measured upper bound on the graphene membrane performance that could be achieved with the nanoporous graphene created here if tears could be completely eliminated. The overall membrane has tears, reducing selectivity, and a support structure with resistance and less than 100% porosity, reducing permeance. Consequently, overall membrane performance is lower. Furthermore, the selectivity measured on this graphene is just above the Knudsen ratio, which is lower than would be needed for most applications. Finally, although these results provide evidence of molecular sieving through large area graphene, the measured performance falls far short of what has been predicted possible, particularly for selectivity. This is illustrated in Fig. 8-18 by comparing the measured graphene performance to simulation predictions. A major contributing factor to the lower measured selectivity is the width of the created pore size distribution; the simulation data assume that a high density of pores can be created with a very specific size and structure. This is difficult to achieve experimentally, particularly over large areas.

8.5 Further development

From the measured graphene membrane performance on AAO supports and model developed based on these results, it is possible to outline the advancements necessary to further improve membrane performance. Further support membrane resistance optimization along with tear and defect sealing can bring the overall membrane performance towards the extracted graphene performance. However, exceeding this performance requires improved pore creation.
methods. Specifically, methods to increase pore density are needed for higher permeance, and
methods to create a narrower pore size distribution are needed to increase selectivity.

The predicted performance improvements that are possible with support resistance tuning
as well as tear and defect sealing are shown in Fig. 8-19 for He / SF₆, H₂ / CH₄, and H₂ / CO₂.
These plots assume the same selective pore size distribution and density obtained in the Fig. 8-16
model fit. The optimal support resistance, maximizing membrane selectivity, was calculated from
the model for each value of graphene coverage. The optimal resistance values are plotted in the
insets. The corresponding overall membrane performance follows the black contour in the main
plot. The blue curves mark the graphene coverage on the AAO. The gray curves show the
performance predictions corresponding to support resistances that differ from the optimal value by
multiplicative constants. These plots show that, even with an optimized support resistance,
significant gains in selectivity will require improved coverage; whereas the current membranes
have ~70% coverage, values of ~95% are needed for large gains. Tear and defect sealing methods
compatible with these AAO supports are therefore desirable, as they will create effectively higher
graphene coverages.

Note that, the maximum selectivity possible in the model (Fig. 8-19a) is higher than the
graphene selectivity measured in Fig. 8-17. The reason for this is that the data in Fig. 8-17 were
extracted assuming that the graphene coverage is the same as that measured prior to ion
bombardment; this estimate includes non-selective tears in graphene that open during plasma
exposure or repeated measurement as part of the graphene performance, rather than excluding
these as tears, as done by the model. This was done so as not to over-report measured graphene
performance.
Improvements in permeance and selectivity possible with higher coverage, higher selective pore resistance, and improved resistance matching are illustrated through the model predictions in Fig. 8-20 to 8-22. These predictions further illustrate that order of magnitude changes to optimize support resistance has little effect on selectivity, whereas improved coverage has great potential to increase membrane selectivity. Increases in selective pore density can be seen to directly translate into increased permeance, while also enhancing selectivity.

Improvements in membrane performance beyond the extracted graphene performance will require advances in selective pore creation methods. The effect of pore density is quantified in Fig. 8-20 to 8-22. Although the gas permeance model for graphene on AAO supports has only been experimentally validated when the pore size distribution is the tail of a log-normal distribution, it was developed for the full distribution. Applying the model when the mean pore size is gas permeable (> d_{He}), the effect of pore size distribution on membrane performance can be estimated. In Fig. 8-23, membrane performance is calculated from the model of Section 8.4.4 for different log-normal pore size distribution parameters. Specifically, each panel in Fig. 8-23b-f shows predictions for different mean values (μ) of pore size, with black contour lines showing different values of the standard deviation (σ) of the pore size distribution. The density of pores with diameter larger than the kinetic diameter of helium is held constant in these plots, and is set to the value obtained in the model fit of Fig. 8-16 (2.6 \times 10^{16} \text{ m}^{-2}). The mean values selected for these plots are less than the kinetic diameter of SF₆, which is desirable for molecular sieving based He/SF₆ separation. The performance is calculated for different values of graphene coverage (γ, gray contours), with the plotted value representing the maximum selectivity possible by optimizing the support resistance.
The predictions in Fig. 8-23 further demonstrate the importance of tear sealing in improving performance; even with a narrow pore size distribution, significant selectivity gains are

Figure 8-19. Model predictions of overall membrane permeance and selectivity for various values of coverage (γ) and multiplicative factors away from the optimal support resistance (c). a, He/SF₆, b, H₂/CH₄, c, H₂/CO₂. Black curve shows values of permeance and selectivity predicted for the optimal support resistance at each γ, with γ increasing along this curve. Contours of constant γ are shown in blue, with the curve tracing increasing factor c, with the support resistance taken as cR_{opt} / R_{AAO}, where R_{opt} is the optimal support resistance at γ and R_{AAO} is the resistance of the 20 nm pore diameter AAO support. Gray contours show permeance and selectivity for constant values of c, with the support resistance of cR_{opt} / R_{AAO} at each γ. The value of γ increases along each contour. The red “x” shows the model fit for the measurements of graphene on a 20 nm diameter pore AAO support (Fig. 8-16). Note that the overall membrane permeance is only for the open area of the membrane; the actual permeance is obtained by multiplying the plotted permeance by the AAO porosity (15%). The model uses the same pore size distribution and density obtained from the fit in Fig. 8-16. Robeson polymer upper bound is from Ref. 4. Insets show the optimal support resistance predicted as a function of graphene coverage.
only observed at high graphene coverages (~95%). At fixed permeable selective pore density, wider distributions are seen to have higher permeance, since the permeance depends on pore area and therefore is more affected by larger pores. However, this also creates more pores that the larger

![Figure 8-20](image)

**Figure 8-20.** Model predictions of overall membrane permeance (a,c,e) and selectivity (b,d,f) for He / SF₆ over various values of support resistance ($R_{\text{support}}$), graphene coverage ($\gamma$) and selective pore density ($\tilde{\rho}_s$). The red "x" shows the model fit for the measurements of graphene on a 20 nm diameter pore AAO support (Fig. 8-16). Note that the overall membrane permeance is only for the open area of the membrane; the actual permeance is obtained by multiplying the plotted permeance by the AAO porosity (15%). The model uses the same pore size distribution obtained from the fit in Fig. 8-16. The presented selective pore density ($\tilde{\rho}_s$) includes only pores larger than 2.6 Å diameter. $R_{AAO}$ is the resistance of the 20 nm diameter pore AAO support. Normalized permeance is the gas flow rate divided by the ideal gas effusion rate through the membrane open area ($A_m \phi$), where $A_m$ is the total measured AAO area and $\phi$ is the AAO porosity.
gas molecule can permeate, reducing selectivity. Thus, in these plots, as the pore size distribution narrows (lower $\sigma$), the permeance decreases and selectivity increases at constant graphene coverage.

Figure 8-21. Model predictions of overall membrane permeance (a,c,e) and selectivity (b,d,f) for H$_2$ / CH$_4$ over various values of support resistance ($R_{\text{support}}$), graphene coverage ($\gamma$) and selective pore density ($\tilde{\beta}$). The red “x” shows the model fit for the measurements of graphene on a 20 nm diameter pore AAO support (Fig. 8-16). Note that the overall membrane permeance is only for the open area of the membrane; the actual permeance is obtained by multiplying the plotted permeance by the AAO porosity (15%). The model uses the same pore size distribution obtained from the fit in Fig. 8-16. The presented selective pore density ($\tilde{\beta}$) includes only pores larger than 2.6 Å diameter. $R_{\text{AAO}}$ is the resistance of the 20 nm diameter pore AAO support. Normalized permeance is the gas flow rate divided by the ideal gas effusion rate through the membrane open area ($A_m \phi$), where $A_m$ is the total measured AAO area and $\phi$ is the AAO porosity.
coverage. Below a certain standard deviation, the selectivity saturates along contours of constant coverage, reflecting that the distribution is sufficiently narrow that the large molecule permeance through selective pores is negligible compared to its leakage flow. These plots provide a

Figure 8-22. Model predictions of overall membrane permeance (a,c,e) and selectivity (b,d,f) for H₂ / CO₂ over various values of support resistance (R_{support}), graphene coverage (γ) and selective pore density (\bar{ρ}_x). The red “x” shows the model fit for the measurements of graphene on a 20 nm diameter pore AAO support (Fig. 8-16). Note that the overall membrane permeance is only for the open area of the membrane; the actual permeance is obtained by multiplying the plotted permeance by the AAO porosity (15%). The model uses the same pore size distribution obtained from the fit in Fig. 8-16. The presented selective pore density (\bar{ρ}_x) includes only pores larger than 2.6 Å diameter. R_{AAO} is the resistance of the 20 nm diameter pore AAO support. Normalized permeance is the gas flow rate divided by the ideal gas effusion rate through the membrane open area (A_m \phi), where A_m is the total measured AAO area and \phi is the AAO porosity.
quantitative tool to estimate membrane performance for particular created pore size distributions and may be useful in developing improved pore creation methods.

Figure 8-23. Model predictions for different log-normal pore size distributions. All distributions are scaled such that the density of pores larger than \( d_{\text{He}} = 2.6 \text{ Å} \) is \( 2.6 \times 10^{16} \text{ m}^{-2} \). 

a, Example pore size distributions for various values of mean (\( \mu \)) and standard deviation (\( \sigma \)). 

b-f, Permeance-selectivity maps for predicted maximum selectivity, obtained by support resistance optimization, for fixed values of \( \mu \), \( \sigma \), and \( \gamma \) (coverage). In b-f, \( \mu = 0.03, 1, 2.5, 3.5, \) and \( 4.5 \text{ Å} \), respectively.
8.6 Conclusions

Methods of selective nanopore generation were explored. High energy ion bombardment, wet and dry etching processes, and low energy ion bombardment followed by etching were considered.

A gas selective macroscopic graphene membrane, attaining Knudsen selectivity, was successfully fabricated by ion bombardment of a three-layer graphene membrane, using a polymer film support. It was postulated that the selectivity of this membrane was resulting from pores larger than the large molecule size, and that creating a high density of smaller pores would be simplified using single-layer graphene. Furthermore, low density ion bombardment followed by etching was adopted as a method more likely to create a uniform pore size distribution.

Single-layer graphene on a resistance matched AAO membrane was bombarded with ions and etched in oxygen plasma. The resulting gas flow measurements show selectivities in excess of the Knudsen selectivity (up to ~8.4 compared to ~6). This is evidence of molecular sieving through nanopores in a macroscopic graphene membrane. From these measurements, the selectivity of the graphene was estimated, in the absence of tears and the support membrane. The resulting permeance and selectivity (up to ~22) are consistent with estimates based on the measured pore size distribution created by this etching method. Further gains in membrane performance will require improvements in defect sealing and methods to create high densities of selective nanopores with narrower size distributions.
Chapter 9

Conclusion

Nanoporous graphene membranes have the potential to exceed permeance and selectivity limits of existing gas separation membranes. However, the performance of macroscopic graphene membranes is inhibited by defects present in large areas of graphene and the availability of methods to generate a high density of selective nanopores. This work focused on the development of macroscopic nanoporous graphene membranes for gas separation applications.

9.1 Summary

The inherent permeance of large areas of graphene was investigated in detail. Micrometer-scale tears and nanometer-scale intrinsic defects were both shown to contribute to leakage through these membranes. It was demonstrated that by stacking multiple layers of graphene, leakage can be reduced exponentially, with more than 99% reductions possible.

A model was developed that accounts for tears and intrinsic defects in graphene and was shown to accurately explain the measured inherent permeance of these membranes. This model attributes leakage to the alignment of tears and defects between layers of graphene. From this, it
was shown that the inherent permeance of multi-layer graphene membranes can be explained with negligible contribution coming from interlayer transport. The analysis was extended to obtain bounding estimates on the interlayer permeance and diffusivity.

Built into the model is the capability to make predictions of overall membrane performance when selective nanopores are introduced. Guided by insights gained from modeling, the membrane design was tuned, using model predictions of performance to evaluate design iterations. From this, membrane designs were obtained for which high overall membrane selectivity was predicted. It was concluded that high selectivity should be possible in macroscopic graphene membranes despite defects in graphene, by careful membrane design.

Fabrication methods were developed to produce a membrane meeting the design specification. These efforts focused on methods to reduce the defect density in graphene, on optimization of the support membrane structure, and on selective nanopore generation methods.

Significant differences in intrinsic defect and tear densities were identified between different graphene sources. It was shown that performing interfacial polymerization on graphene membranes to form polymer plugs over tears is a viable method to reduce leakage in graphene membranes. The potential of atomic layer deposition to seal nanometer-scale defects in graphene to gases, while leaving large areas of pristine graphene available for selective pore generation, was further demonstrated.

Optimization of the support membrane design can further reduce the effects of tears and defects in graphene. Choosing a support membrane with a similar resistance to that due to selective nanopores in graphene will prevent leakage through tears from dominating gas transport while not unnecessarily reducing membrane permeance. Furthermore, selecting a characteristic pore size or
layer thickness that is smaller than the spacing between intrinsic defects can isolate their effect to a small fraction of the membrane area.

Two adequate support membrane structures were developed. The first consisted of a thin (~1.5 μm), permeable polymer film. The resistance of this support was found to be too high for use with single-layer graphene, but acceptable for three-layer membranes. It was shown that polymer spin coating resulted in filling of support pores beneath tears, having the added benefit of locally increasing the resistance where tears exist in the membrane. The second structure consists of 20 nm diameter, 50 μm long, isolated pores with constant cross section throughout the membrane (AAO membranes). The graphene permeance estimated for selective pores in an area over these pores is well matched to the permeance resulting from Knudsen diffusion in the pore.

Knudsen selectivity was achieved with macroscopic porous graphene membranes by ion bombardment of three-layer graphene with a polymer layer for resistance matching. It was postulated that at the bombardment densities required to create measureable permeance in these membranes, significant damage to the graphene had occurred. The measured selectivity likely resulted from Knudsen effusion through pores larger than the diameter of both gas molecules.

Using single-layer rather than multi-layer graphene was expected to simplify the process of generating a high density of small nanopores. Furthermore, methods employing low density ion bombardment to nucleate defects followed by etching to enlarge them into selective nanopores were expected to yield a more uniform pore size distribution. Single-layer graphene on 20 nm diameter pore AAO supports was bombarded with ions at a low density and then etched in oxygen plasma. Selectivities in excess of the Knudsen effusion limit (~8.4 compared to ~6.0) were attained, providing evidence of molecular sieving based gas separation through macroscopic graphene membranes. Gas permeances and selectivities in the absence of tears and the support
layer, were extracted from these measurements. Graphene selectivities of ~22 were achieved. These results are consistent with estimated graphene permeance and selectivity based on generated pore size distributions measured by STEM imaging.

9.2 Recommendations and future work

Improving overall membrane selectivity will require improvements in leakage sealing methods and selective nanopore generation. The graphene selectivity and permeance obtained by oxygen plasma etching single-layer graphene on AAO supports are consistent with the measured selective nanopore size distribution. The graphene selectivity of ~22 is higher than the achieved overall membrane selectivity of ~8.4. The overall membrane selectivity can be increased to near the graphene selectivity by sealing tears in these membrane. Lower defect density graphene or methods to transfer large areas of graphene with smaller tear densities would also improve performance. However, increasing the selectivity even further will require methods to create selective nanopore size distributions that give graphene higher selectivity. The width of the generated nanopore size distribution imposes this limit on the membrane selectivity.

The AAO support membranes used in these experiments are relatively brittle, expensive, and limited in size. A flexible polymer support membrane may be better suited for commercialization of these membranes. One possible option is to etch PCTEMs to have a more uniform pore diameter throughout the cross section, rather than a significantly smaller diameter on the surface than in the bulk. The pore structure need not be completely uniform, as long as the pores are etched all the way through, have sufficiently small diameter, and do not have a significantly smaller diameter on the surface. These supports may be more practical and may also improve the graphene transfer yield.
Defect sealing approaches such as interfacial polymerization and atomic layer deposition can reduce leakage. However, when forming on and around nanometer-scale defects in graphene, it is unclear exactly where these materials will form and what their structure will be. For example, the thickness, porosity, and defectiveness of the deposited materials will be important. Understanding the formation process and resulting structure will help to improve these sealing methods and refine membrane transport models.

Methods to create a high density of sub-nanometer pores with a narrow size distribution will be needed if high selectivities are to be achieved in large areas of graphene. Possible methods include bombardment with ion clusters or buckyballs, or growth of selective pores into the two-dimensional material during synthesis.

There is little experimental data on the effect of selective pore terminal groups on graphene membranes. Characteristics of chemical groups on the pore perimeter including partial charge, flexibility, and affinity to gas molecules could have a significant effect on transport. It would be useful to investigate the precise pore structures created by different methods. Furthermore, differences in the structure of pores created in few-layer graphene as compared to single-layer graphene may be significant and could be explored.

Gas separation simulations have predicted a significant contribution of an adsorption pathway to transport. In cases where the larger molecule is preferentially adsorbed, this can reduce selectivity. Experiments in which gas transport is measured on small areas of graphene over a range of temperatures and pressures could distinguish the contribution of adsorptive from ballistic transport and corroborate these predictions. Phenomena such as adsorption could result in different membrane permeances for gases in a mixture than measured in single species experiments.
Measurements of membrane performance for gas mixtures will be necessary to determine the importance of this effect.

Graphene membrane permeance was observed to gradually decrease with time, suggesting that selective pores may become obstructed by contaminants in the gas or on the membrane. Further investigation is needed to determine whether this will limit the useful life of graphene membranes or if there are effective cleaning processes to restore membrane performance.

Only a few experimental papers have been published on graphene membranes. However, a comparatively large number of simulation studies have been performed to predict the performance of various nanopore structures for different gas molecules. There are still several outstanding questions related to graphene membranes that simulations could provide significant insights into, particularly on some of the more practical aspects of membrane operation.

Most graphene nanopore transport simulations fix the carbon atoms. However, graphene is flexible, and can deform due to forces exerted by gas molecules passing through pores in the graphene. Furthermore, random thermal motion of carbon atoms cause continuous changes in pore size. Incorporating these factors into transport simulations could reduce predicted gas selectivities by many orders of magnitude. Simulations to clarify this issue would be informative. It would also be beneficial to simulate gas transport through nanopores with experimentally observed geometries and terminal groups, as opposed to imagined structures.

To mitigate leakage, multi-layer graphene membranes are common in experiments; insight could be gained from simulations to determine how this added thickness affects transport. Ion-bombardment is a common method of selective nanopore creation, and simulations of this process could identify how having more than one layer of graphene changes the pores that are created and the optimal bombardment conditions. Simulations of pore size created by ion cluster or buckyball
bombardment could similarly test the feasibility of these methods and optimize the pore creation parameters.

When viewed in a transmission electron microscope, experimentally fabricated graphene membranes often have large fractions of their surface covered in contamination. It is possible that this contamination will tend to stick to small selective pores in graphene, preventing transport through highly selective areas. Simulations of the dynamics of polymer contamination on graphene membranes could determine whether this is a concern.

Recent experiments of gas and ion transport through single graphene nanopores show random changes in permeance between discrete values over time. Simulations could be helpful in understanding this behavior. For example, it would be interesting to explain why the characteristic permeance switching time is different in ion and gas transport, and why the behavior is reported for gas transport through single-layer membranes but not two-layer membranes.

9.3 Perspective

A large number of simulations have predicted that graphene has the potential to provide order of magnitude improvements in gas separation membrane performance. However, despite predictions of two-dimensional material membrane gas selectivities of up to $10^{78}$ (Ref. 44), even a low level of defects in graphene membranes will limit their use to separations with modest purity requirements. Due to similar challenges, conventional membranes are often not the method of choice for high purity separations.\textsuperscript{1-3,126} Therefore, provided that selectivities of approximately 50-100 can be achieved, graphene could significantly advance membrane performance through the permeance increases enabled by an atomically thin active layer.
Low permeance can make membranes impractical for high throughput gas separation processes, such as in high production rate natural gas treatment plants or low pressure carbon capture processes.\textsuperscript{1-3,126} Graphene’s high permeance could expand the industrial use of membranes for gas separation processes. However, doing so will require significant further advances in graphene membrane technology.

Graphene membrane gas selectivity has only been achieved in lab-scale systems.\textsuperscript{12,33,78} Material defects are a major obstacle to scaling graphene membranes up to practical sizes. This thesis has largely focused on developing methods to address defects, leading to measurable gas selectivity on centimeter-scale membranes. However, further improvements in the quality of large areas of graphene and more effective methods to seal defects are needed to produce large-area graphene membranes with sufficiently high selectivities for practical gas separation systems. Improvements in these areas have the greatest potential for immediate gains in graphene membrane performance.

Graphene membranes have been produced with high selectivity but prohibitively low permeance, and with high permeance but low selectivity.\textsuperscript{12,33} Methods to create a high density of small pores are needed to simultaneously realize high permeance and high selectivity. In this thesis, a process was developed and shown to produce pores suitable for gas molecule sieving in centimeter-scale areas. The performance of just the areas of the membrane with graphene was shown to be comparable to the Robeson limit for H\textsubscript{2}/CH\textsubscript{4} and to exceed this limit for H\textsubscript{2}/CO\textsubscript{2}. However, the overall membrane, containing tears and a support structure with less than 100\% porosity, has performance closer to the Robeson limit. Furthermore, the performance achieved is significantly lower than has been predicted possible for graphene.
Overall membrane performance can be increased to near the measured graphene performance by defect sealing, but improved pore creation methods will be needed to exceed this performance. Methods to create a higher density of selective pores are needed to reach higher membrane permeance, and methods to create a narrower pore size distribution are need to attain higher selectivities. The pore size distribution needs to be very narrow for many gas separations. The stochastic nature of defect nucleation and growth makes it difficult to obtain precise control over pore size by etching graphene. Growing pores into the two dimensional material prior to transfer may afford better control over the pore size distribution. For example, using intrinsically porous two-dimensional graphene-like materials, such as graphdiyne, which has been synthesized on millimeter scales, may provide this level of control. The pores in such materials are defined by the chemical structure, so have a very narrow size distribution, and can have significantly higher densities than achieved in graphene.

Even with a very narrow pore size distribution, some separation processes may be difficult by size exclusion alone. For example, O$_2$ / N$_2$ have kinetic diameters of 3.4 Å / 3.6 Å, and CO$_2$ / N$_2$ have kinetic diameters of 3.3 Å / 3.6 Å. However, for CO$_2$ separations in particular, it may be possible to tune the membrane selectivity by functionalizing the pore rim or graphene surface. Simulations suggest that the electrostatic moment of CO$_2$ can cause strong interactions with such functional groups, influencing its permeance.

Graphene gas separation membranes have been under development since 2008, when it was shown that pristine graphene is impermeable to gases. During this time, a number of simulations have quantified the potential performance gains possible with this membrane material. High selectivity gas molecule sieving was demonstrated through a single sub-nanometer size pore in graphene and high gas permeance has been demonstrated through an array
of 7.6 nm pores in graphene. This thesis has focused on major issues in graphene membrane scalability. Specifically, the development of methods to address defects in graphene and to produce sub-nanometer-scale pores with high density resulted in measureable gas selectivity over large areas. Further advances in these aspects of membrane fabrication are still needed to attain membrane performance on the level and scale required for practical separation systems. Although the remaining challenges in developing this technology are demanding, graphene membranes will significantly benefit industrial separation processes if their full potential is realized.
Appendix A

Compiling graphene gas transport data

Figures 2-4, 2-10, and 8-18 provide compilations of published graphene membrane and NATM gas transport data. This appendix describes how the simulation and experimental data were extracted from the literature to construct these figures.

A.1 Extraction of pore area (simulations)

For consistency, pore areas were calculated from simulation data using one consistent definition introduced by Sun et al.\textsuperscript{70} Specifically, the pore area is defined as the open area in the plane of the pore where the atoms lining the pore edge are taken to be hard spheres with diameter equal to the van der Waals diameter of that atom, $D_{vdw} = 2R_{vdw}$, divided by $\sqrt{2}$. The factor of $1/\sqrt{2}$ accounts for the fact that some incident molecules that collide with pore rim atoms are deflected into the pore rather than reflected away.\textsuperscript{70,79}

Data from literature reports were processed as follows. First, coordinates of the lattice and pore atoms were extracted from each study. Where possible, reported coordinates were used directly. Otherwise, the coordinates were digitally extracted from images of the pore geometry.
High resolution black and white images of the pore with the effective molecule diameters (i.e. divided by $1/\sqrt{2}$) were produced (e.g., Fig. 2-8a). The pore area was then computed as the area occupied by the white pixels. The effective pore diameter was defined as the diameter of a circle with the same area as the pore, i.e., $D_p = \sqrt{4A_p/\pi}$.

A.2 Extraction of pore area (experiments)

The pores created by Celebi et al.12 (diameter greater than 7 nm), are sufficiently large that no effective pore diameter correction was required. The pores measured by Koenig et al.33 and Wang et al.78 were not imaged. For these, it was assumed that a single pore was responsible for the observed transport and the pore diameter was taken to be equal to the size cut off, that is, the kinetic diameter of the smallest molecule that could not permeate the pore.

A.3 Pore permeance

If computed in the study, the reported rates of transport were taken directly from text, tables, or figures. If necessary, the simulation pressure and porosity were used to convert transport rates into pore permeation coefficients or effective area. For normalization, the relevant ideal gas flux ($J_{\text{ideal gas}}$, Box 1-1) was calculated at the simulation temperature (often 300 K). When simulations only calculated energy barriers without using a temperature, the pore permeation coefficient or effective area was calculated from the energy barrier assuming a temperature of 300 K, as described below.

If transport rates were not directly reported in molecular dynamics simulations, they were calculated from the number of molecule crossings over the simulation time. For simulations in which molecules of one species were initially placed on both sides of the membrane at the same
partial pressure, the number of molecule crossings in both directions was divided by two to obtain the equivalent single direction flux for the dilute gas.

In *ab initio* studies, if permeance values were not directly reported, they were estimated from reported energy barriers by the method of Schrier\textsuperscript{38} using Eq. 2-3. Although the energy barrier is not constant over the pore, the pore permeation coefficient is estimated by further multiplying by the pore area, $A_p$. This results in an upper bound on the pore permeation coefficient.

Selectivities were calculated as the ratio of permeance values. Some *ab initio* studies calculate the selectivity as a ratio of Arrhenius factors of energy barrier (Eq. 2-1) instead. In these cases, the permeance was estimated from Eq. 2-3, and used to re-compute selectivity.

For molecular dynamics studies, it is common to observe no large molecule crossings in a simulation, due to the limitation on the length of time that can be simulated by this approach. In these cases, the data are omitted unless the selectivity was also estimated from the energy barrier.

### A.4 Pressure estimation

Adsorption of gas molecules on the NATM surface has the effect of reducing the pressure in the bulk gas. This results in a lower rate of incidence of gas molecules from the bulk on the pore. Many studies adjust for this reduction in the driving force. When results were not corrected for this effect and data were available, this effect was corrected for by using the average number of adsorbed molecules and size of the adsorption layer to determine the volume of the bulk region and the average number of molecules in the bulk gas. These values were used in the ideal gas law to calculate the pressure in the bulk. If the number of adsorbed molecules was not reported, the number of adsorbed molecules and the size of the adsorption layer were estimated from simulation snap shots, if they were presented.
Simulations in which gas molecules are initially placed on one side of the membrane require careful treatment because the pressure difference across the membrane decreases over time. Some studies correct for this by using the average pressure difference over the simulation or fitting an exponential decay function to the crossings versus time data. For simulations that did not correct for this, the permeance was taken over a time where the crossings versus time data were reasonably linear, and the average of the initial and final pressure differences was used.

For simulations in which gas molecules were initially at equal partial pressure on both sides of the membrane, the absolute partial pressure in the bulk was used instead of the difference across the membrane. However, as explained above, the number of molecule crossings in both directions was divided by two to calculate the equivalent one way pressure-driven flux across the membrane. In some simulations, the driving force for flow across the membrane is due to an imposed body force. In these cases, the equivalent pressure is calculated by adding to the ideal gas pressure of the system the product of the force per molecule, the number of molecules upstream of the membrane, and the inverse of the membrane area.

### A.5 Membrane Permeance

For studies on two-dimensional materials with inherent porosity that did not explicitly report the pore density, its value was calculated from the extracted atom coordinates. For Fig. 2-10 and 8-18, pore permeance coefficients were converted to membrane permeance using the intrinsic porosity if the material was inherently porous. For materials that were not intrinsically porous, a pore density of $10^{12}$ cm$^{-2}$ was assumed in the conversion.
Appendix B

Gas permeance measurement methods

Details of the systems and procedures used to perform gas flow rate measurements on graphene membranes are provided in this appendix.

A schematic of the gas flow rate measurement apparatus is sketched in Fig. 3-1. The membrane is sealed between an upstream pressure line and a downstream reservoir. A vacuum pump is used to evacuate the gas lines upstream of the membrane and the reservoir downstream of the membrane. The gas lines upstream of the membrane are connected to a gas cylinder with a regulator set at 1 atm absolute pressure. Measurements are acquired by opening the valve connecting the downstream side of the gas cylinder’s regulator to the lines upstream of the membrane, pressurizing the upstream side of the membrane to 1 atm with a single gas species.

During measurements, the upstream line was continuously supplied with a single gas species at an absolute pressure of 1 atm by a regulated gas cylinder. A pressure transducer was used to measure the rate of pressure rise in the downstream reservoir, resulting in time traces such as those presented in Fig. 3-2b.
For every flow rate measurement, pressure data were acquired until the downstream reservoir pressure increased from 0.00 psia to 0.50 psia. The slope of the pressure-time data, \( \dot{P} \) [Pa/s], is computed by a linear least-squares fit. The flow rate is then calculated from the ideal gas law,

\[
\dot{n} = \dot{P} \frac{V}{RT}
\]  

(B-1)

where \( \dot{n} \) [mol/s] is the molar flow rate, \( V \) [m\(^3\)] is the downstream reservoir volume, \( \bar{R} \) [J/mol-K] is the universal ideal gas constant, and \( T \) [K] is the temperature.

### B.1 Measurements of graphene on PCTEMs

The apparatus used to measure gas flow rates through graphene on a polycarbonate track-etched membrane (PCTEM) is drawn in more detail in Fig. B-1. A photograph of this system is provided in Fig. B-2c. In preparing for gas flow rate measurements, the membrane is placed on a sintered steel support and sealed between two flanges. For 1.0 \( \mu \)m pore PCTEMs, a sintered steel support capable of filtering 40 \( \mu \)m diameter particles was used to accommodate the relatively high flow rates through these membranes without adding significant resistance to flow behind the membrane. For smaller pore diameter PCTEMs (10 nm to 200 nm), sintered steel supports capable of filtering 2 \( \mu \)m diameter particles were used. These supports are smoother, potentially reducing damage to the membrane by the support.

The pressure transducer used to monitor the pressure in the downstream reservoir with time has a resolution of 0.01 psi. The size of the downstream volume, \( V \), can be reduced from approximately 115 L to 4 L by closing a valve that separates the two downstream reservoirs. This allows for a wide range of flow rates to be measured with acceptably short measurement times of less than one hour.
Figure B-1. Drawing of gas flow measurement setup for graphene on PCTEM.

PCTEM supported membranes with very low flow rates are measured on the system drawn in Fig. B-3c. Photographs of the system and membrane mounting are provided in Fig. B-2a. A valve in this system expands the downstream volume from approximately 7 mL to 30 mL. This volume was connected to the system in Fig. B-1 to calibrate the volume ratios of the various reservoirs. Membranes are mounted in a similar configuration as in Fig. B-1, as shown in Fig. B-3e.

Membranes with polymer film coatings have lower flow rates than membranes without a coating and are mounted as shown in Fig. B-3d to reduce leakage further. A thin film of epoxy is used to seal the membrane to a piece of aluminum foil tape, leaving the measurement area exposed. After curing, the tape is placed over the sintered steel support seated on the downstream flange. An O-ring in a groove on the upstream flange seals it on the tape. This approach allows for strong clamping forces to seal the flanges, without these forces being exerted on the membrane. The pressure transducer installed on this system has a resolution of 0.0001 psi.
B.2 Measurements of graphene on AAOs

The measurement setup for graphene on anodic aluminum oxide support membranes (AAOs) is shown in Fig. B-2b,B-3a,b. The system is similar to that used for graphene on PCTEMs, but avoids clamping stresses that could fracture these brittle membranes. The membrane holder was obtained from InRedox. The membrane is supported by a porous disk. An O-ring clamps directly on the membrane from the upstream side. A disk with a hole in the center and another O-ring sit on top of this, providing adaptation for 10 mm diameter AAO disks to a setup that can also be used on 25 mm diameter AAO disks. The upstream flange has an angled surface that clamps against the top O-ring to seal the system.

The volume downstream of the membrane holder is approximately 500 mL, reducible to 7 mL by closing a valve. This volume is equipped with a pressure transducer with 0.0001 psi resolution.

Figure B-2. Photographs of gas flow rate measurement setup and membrane mounting process. a, Low flow rate PCTEM measurement system. b, AAO measurement system. c, Standard PCTEM flow rate measurement system.
**B.3 Measurement system verification**

Flow rates through bare PCTEM with various pore sizes measured using the setup shown in Fig. B-1 are plotted in Fig. 3-2d,e. The flow rates obtained for nitrogen agreed with manufacturer specified flow rates to within their reported uncertainty in polycarbonate pore density, helping to verify the measurement setup.

The nitrogen flow rate through a bare polycarbonate membrane without track-etched pores was also measured. Zero flow rate was observed over a 24 h period, to within the resolution of the pressure transducer, verifying that the downstream reservoir was properly sealed and that the gas permeance through polycarbonate was negligible for these experiments.

![Diagram of measurement setups](image)

**Figure B-3.** Gas flow rate measurement setups for flow rate measurements. a, AAO membrane measurement system and b, membrane mounting. c, Low flow rate PCTEM measurement system, d, epoxy mounting, and e, standard mounting. In the metal foil and plate, the central hole is aligned with the membrane and defines the area available to gas flow, whereas the six surrounding bolt holes are for clamping the flow cell together once the membrane has been mounted.
In order to determine whether using a linear resistance model for gas flow in polycarbonate pores was reasonable, nitrogen flow rates through a PCTEM with 1 μm diameter pores were measured at different upstream pressures within the operating range of the system. The approximate linearity of the flow rates with pressure over this range, seen in Fig. 3-2c, suggests that this approximation is reasonable.
Appendix C

Experimental uncertainty estimates

The error bars presented in Fig. 8-3, 8-12 to 8-17, were estimated as outlined in Table C-1. The largest sources of error in measured membrane permeance are the uncertainty in the downstream volume of the flow cell, used in the ideal gas law to determine the flow rate, and uncertainty in the measured membrane area due to compression of the gasket during membrane mounting. Normalized flow rates and selectivities are not affected by the error in the downstream volume since this volume is the same in all measurements. Furthermore, the variability in membrane area between measurements is significantly smaller than the uncertainty in the absolute value of the membrane area. This was assessed by repeated clamping of the same membrane and measuring flow rates.

Uncertainty in setting the upstream pressure is an important source of error in measuring normalized flow rates and selectivities, as flow rates scale with this value. Other factors affecting error in normalized parameters include uncertainty in the pressure transducer measurement, resulting from measured flow cell leakage, and non-linearly in the pressure-time history.
Table C-1. Experimental uncertainty estimates.

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Uncertainty (±)</th>
<th>Membrane permeance</th>
<th>Membrane normalized permeance</th>
<th>Membrane selectivity</th>
<th>Graphene permeance</th>
<th>Normalized graphene permeance</th>
<th>Graphene selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainty in downstream volume of flow cell</td>
<td>20%</td>
<td>✓</td>
<td>—</td>
<td>—</td>
<td>✓</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Uncertainty due to pressure transducer error (slope of pressure - voltage calibration curve, discretization error, least squares fitting for slope)</td>
<td>2%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Flow cell leakage</td>
<td>0.2%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Membrane area uncertainty due to gasket deformation during membrane mounting</td>
<td>20%</td>
<td>✓</td>
<td>—</td>
<td>—</td>
<td>✓</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Uncertainty in upstream pressure</td>
<td>3%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Neglected non-linearly of measured pressure-time curve</td>
<td>2%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Membrane fouling during gas measurement</td>
<td>0.5%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Uncertainty in membrane porosity</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Error accumulation in calculations using multiple measurements</td>
<td>—</td>
<td>—</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>28.7%</td>
<td>5.9%</td>
<td>5.9%</td>
<td>31.1%</td>
<td>8.3%</td>
</tr>
</tbody>
</table>
Extracted graphene normalized permeance and selectivity have higher error than membrane normalized permeance and selectivity due to the uncertainty in AAO porosity that affects the calculation.

The various sources of measurement error were combined to estimate the total measurement uncertainty\textsuperscript{128} of reported permeance and selectivity as reported in Table C-1.
References


29. Li, H., Song, Z., Zhang, X., Huang, Y., Li, S., Mao, Y., Ploehn, H. J., Bao, Y. & Yu, M.


