Gas permeation through double-layer graphene oxide membranes: The role of interlayer distance and pore offset

Quan Liu\textsuperscript{a}, Krishna M. Gupt\textsuperscript{a}, Qisong Xu\textsuperscript{b}, Gongping Liu\textsuperscript{a,⁎}, Wanqin Jin\textsuperscript{b,⁎}

\textsuperscript{a} State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 5 Xinnan Road, Nanjing 210009, PR China
\textsuperscript{b} Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576, Singapore

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\textbf{ABSTRACT}

Hierarchically stacked graphene oxide (GO) membranes have sparked considerable interest due to their prominent separation performance; however, the underlying separation mechanisms remain elusive. In this study, we conducted molecular dynamics (MD) simulations to explore the role of interlayer distance and pore offset in gas (H\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2} and CO\textsubscript{2}) permeation through double-layer GO membranes. Gas permeance is found to increase with the interlayer distance and pore offset until the interlayer distance exceeds a critical value. With elongating the interlayer distance and pore offset, a sieving effect occurs to overcome preferential adsorption and dominates the transport in mixed H\textsubscript{2}/CO\textsubscript{2}, resulting in selective permeation shifting from CO\textsubscript{2} to H\textsubscript{2}. This simulation study provides mechanistic insight into gas permeation through layered GO membranes, and would facilitate the design of new GO membranes for high-performance gas separation.

1. Introduction

With unique 2D microstructure, GO membranes have received significant attention for desalination \cite{1,2}, water treatment \cite{3,4} and gas separation \cite{5,6}. Together with pore size \cite{7}, pore environment \cite{8}, lateral dimension \cite{9}, and ratio of O/C \cite{10}, interlayer distance and pore offset of GO membrane influences permeance directly. By varying d-spacing, a highest water permeation flux was achieved in crosslinked GO laminate membranes \cite{11}. Via tailoring interlayer-galleries by vacuum-spin technique, GO membranes exhibited remarkable separation performance for H\textsubscript{2}/CO\textsubscript{2} and H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6} gas pairs \cite{12}. A larger pore offset can significantly promote salt rejection \cite{13}. On other hand, misaligned pore provides more permeation pathway to a certain extent and even introduces transport resistance. A number of experimental and theoretical studies have been conducted to understand the separation mechanisms, especially for liquid separation \cite{14-17}. In contrast, the study on gas separation through GO membranes is relatively limited \cite{18}.

Although outstanding separation performance was reported for gas separation using GO membranes, the mechanism is not completely understood especially for mixed gas H\textsubscript{2}/CO\textsubscript{2}. For instance, intrinsic defects in GO membranes contributed to an excellent H\textsubscript{2} selectivity for H\textsubscript{2}/CO\textsubscript{2} separation \cite{6}, highly interlocked GO membranes exhibited a high CO\textsubscript{2} permeability \cite{5} and selectivity over H\textsubscript{2} due to the preferential CO\textsubscript{2} adsorption in layered GO membranes. This reverse selectivity of mixed gas H\textsubscript{2}/CO\textsubscript{2} was presumably attributed to the competition of sieving effect and preferential sorption on the gas transport through layered GO membranes, which can be controlled by interlayer distance and pore offset.

In this context, we carried out molecular dynamics (MD) simulations to examine gas permeation through double-layer GO membranes with a variable of interlayer distance and pore offset and focused on the qualitative mechanism understanding. The permeance of pure gas (H\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2} and CO\textsubscript{2}) with these two factors fell into a regular rule: larger interlayer distance and greater pore offset promote gas permeation till bulk behavior occurs. Interlayer lateral diffusion of gas illustrated the effect of pore offset. Radial distribution function (RDF) analysis was used to compare the affinity between GO membranes with four gases. For mixed gas H\textsubscript{2}/CO\textsubscript{2} separation, lateral diffusion coupled with density distributions and trajectories were used to illustrate a reverse gas selective permeation and predicate the dominant separation mechanism (sieving effect or preferential adsorption) through layered GO membranes with different interlayer distance and pore offset.

2. Models and methods

In our GO models, the hydroxyl and epoxy groups are attached to the basal plane and carboxyl groups are grafted in the defect regions. All the oxygen-containing functional groups are randomly distributed on both sides of GO surfaces. The numbers of epoxy, hydroxyl and...
carboxyl groups are 79, 65 and 4, respectively, following our recent experimental studies [19]. The charge of each atom in oxygen functional groups is adopted from the model used by Xu et al. [20] and all the sp$^2$ carbons in our models are uncharged. The GO sheets were constructed by Amorphous Cell in Materials Studio. Energy minimization was performed with 5000 iterations and 5.0 $\times$ 10$^{-6}$ convergence, and the geometric structure of GO sheets were optimized by Forcite module with ultrafine quality. As already used in GO simulation [21], the GO sheets were mimicked by the COMPASS [22] force field including Lennard-Jones (LJ) and electrostatic potentials, 

$$U = \sum_{ij} 4\varepsilon_{ij} \left[ \left( \frac{r_{ij}}{\sigma_{ij}} \right)^{12} - 2 \left( \frac{r_{ij}}{\sigma_{ij}} \right)^6 \right] + \sum_{ij} \frac{q_i q_j}{4\varepsilon_0 r_{ij}} \quad (1)$$

where $\varepsilon_{ij}$ and $\sigma_{ij}$ are the well depth and collision diameter, $r_{ij}$ is the distance between atoms $i$ and $j$, $q_i$ is the atomic charge of atom $i$, and $\varepsilon_0 = 8.8542 \times 10^{-12}$ C$^2$ N$^{-1}$ m$^{-2}$ is the permittivity of vacuum. After energy minimization and structure optimization, GO sheets were a bit wrinkled and were used as the initial structure for MD simulations. Fig. 1(a) shows the configuration of two GO sheets with a misaligned pore. Pore offset is denoted by a cylinder between the entrance and exit in the upstream and downstream graphene layer. And its value is defined in Fig. 1(b) in the same xy plane, which is the distance between the exit pore and the shadow of the entrance pore. The pore size was estimated by plotting atoms as van der Waals spheres and its diameter was calculated by the formula $d = 2\sqrt{(A/\pi)}$ [7]. Here, we constructed these GO sheets with a very small pore size of about 3.0 Å to mimic the perfect GO membranes with no or only a few defects. In the pore region, the numbers of epoxy and carboxyl groups were set as 19 and 4, respectively. Fig. S1 shows the pore size and pore chemistry. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.seppur.2018.07.044.

The configuration of a simulation system for gas permeation and separation is illustrated in Fig. 1(c). There are two chambers, one is a gas reservoir containing 200 molecules and the other is a vacuum, separated by 3 $\times$ 3 nm$^2$ double-layer GO. These GO sheets are vertically aligned in the center of the simulation cell. The interlayer distance between the geometric centers of two GO layers and pore offset varied from 0.8 nm to 1.4 nm and from 0.0 nm to 2.1 nm, respectively. Additionally, the left graphene plate is exerted an external force along the z direction. The acceleration rate ($a$) of graphene is calculated from the applied pressure ($P$), $P = Nma/A$, where $N$ is the total number of carbon atoms in the graphene and $A$ is the cross section area of the graphene. This pressure-driven operating condition is wildly used in non-equilibrium MD simulation for pervaporation [23], desalination [24–26] and reverse osmosis [27,28]. With this exerted acceleration, the left graphene can self-adjust its position.

**Fig. 1.** (a) Configuration of two GO sheets with misaligned pores; (b) pore offset is the distance between the exit pore and the shadow of the entrance pore in the same xy plane. Blue: C, white: H, red: O atom; (c) A simulation system for gas permeation through a GO membrane. A gas mixture containing 100 H$_2$ and 100 CO$_2$ and a vacuum chamber are on the left and right of the membrane, respectively. The left graphene plate is exerted under a pressure of 184 bar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
During simulation, and then pushes gas molecules to permeate through the GO membrane. Noted that experimental pressure values are smaller than the applied pressure here. This is a common practice in non-equilibrium MD simulation [29–31] to reduce the thermal noise and enhance signal/noise ratio within a nanosecond timescale [24]. The periodic boundary conditions are applied in all the three directions to mimic an infinite system. Another graphene plate is fixed in the right vacuum chamber to avoid gas moving between periodic cells.

Before MD simulation, the system was firstly subjected to energy minimization using the steepest descent method with a force tolerance of 1 kJ/(mol·Å) and a maximum step size of 0.1 Å. Then, velocities were assigned based on the Maxwell-Boltzmann distribution at 300 K. Thereafter, MD simulation was performed in a canonical ensemble (NVT). The velocity-rescaled Berendsen thermostat [32] was used to maintained temperature at 300 K with a relaxation time of 0.1 ps. A time step of 1 fs was carried out to integrate the classical equations of motion by using leapfrog algorithm. A cutoff of 12 Å was used to calculate the Lennard-Jones (LJ) interactions and Particle-Mesh-Ewald method was subjected to evaluate long-range electrostatic interactions with grid spacing of 1.2 Å and a fourth-order interpolation [33]. In our GO models, we chose the partial of unchanged C atoms that haven’t been grafted any functional groups to exert the position restriction, while other atoms were flexible. And the percentage of restricted C atoms is 7% compared to GO atoms. Gas molecules were allowed to move freely during the simulation. The simulation duration was 20 ns and the trajectory was collected every 1 ps for analysis. GROMACS package v.4.5.3 was used to conduct the simulation [34].

3. Results and discussion

3.1. Gas permeation

The separation performance is evaluated by monitoring the number of permeated gases into the vacuum chamber. Fig. S2 presents the time evolution of the permeated pure gas CO₂ through GO membranes with 0.9 nm interlayer distance and a variable pore offset. By fitting the linear slope, CO₂ permeance obtained in GO membranes with various interlayer distances and pore offsets is shown in Fig. 2. The corresponding ideal selectivity is shown in Fig. S3.

Obviously, CO₂ permeance increases with interlayer distance and pore offset, and it becomes independent of these two factors as long as interlayer distance is larger than 1.1 nm. Not only larger interlayer distance but also greater pore offset can excavate a wider spacious space for facilitating gas lateral diffusion. Via analyzing CO₂ diffusion along the plane of the pore within GO interlayer galleries, the diffusion coefficient \(D_{xy}\) is calculated from the mean square displacement (Eq. (2)) and Einstein equation (Eq. (3)),

\[
MSD_{xy}(t) = \frac{1}{N} \left( \sum_{i=1}^{N} \left[ x_i(t) - x_i(t_0) \right]^2 + \left[ y_i(t) - y_i(t_0) \right]^2 \right)
\]

\[
D_{xy} = \lim_{t \to \infty} \frac{dMSD_{xy}(t)}{dt}
\]

where \(\left[ x_i(t) - x_i(t_0) \right]^2 + \left[ y_i(t) - y_i(t_0) \right]^2\) is the mean square displacement parallel to the plane of pore within GO interlayer galleries and \(N\) is the number ofatoms.
number of CO2 molecules. Dxy is determined by the linear slope of the curve during the time interval \( t = 0-50 \text{ ps} \) via the Einstein equation.

By taking the case of \( d = 0.9 \text{ nm} \) and 1.2 nm as a representative, CO2 lateral diffusion coefficients within interlayer galleries and the equilibrium configurations of the membranes are presented in Fig. 3. Longer pore offset promotes CO2 translational movement in GO membranes when interlayer distance lower than the critical value (\( D = 1.1 \text{ nm} \)), which results in higher CO2 permeance in Fig. 2(a). Above the critical value of interlayer distance, the diffusion properties are invariable in the case of 1.2 nm interlayer distance due to bulk behavior occurs [29]. The aligned interlayer gallery (Fig. 3(a)) accommodates only one CO2 molecule. This trapped CO2 has a very limited lateral diffusion and becomes an obstacle for latter molecules crossing into the entrance, resulting in a low permeance. On the contrary, misaligned pores introduce faster CO2 lateral diffusion in GO membranes so that the trapped CO2 can shift away from the entrance, which offers less resistance for latter gas molecule entering into. More CO2 molecules are accommodated in GO membrane interlayer gallery in Fig. 3(b)–(d). Thanks to faster interlayer lateral diffusion, higher gas permeance is obtained with longer pore offset. Larger interlayer distance also introduces a good lateral diffusion in GO membranes. With 1.2 nm interlayer distance, more than one CO2 layers are appeared in interlayer galleries (Fig. 3(e)) and this bulk behavior leads interlayer lateral diffusion of CO2 invariable with pore offset.

Except for CO2, the permeation behavior of H2, CH4 and N2 also follow the above rules. Thanks to the weak interaction with GO membranes, H2, CH4 and N2 molecules move quickly through GO membranes and their bulk behaviors are showing up earlier at O = 2.1 nm, which results in the permeance of H2, CH4, N2 independent with interlayer distance at fixed pore offset 2.1 nm. While stronger affinity make CO2 stay longer and significantly affected by pore offset in interlayers. The free pathway offered by 2.1 nm pore offset is far from enough to arouse its bulk behavior. So interlayer distance is still dependent with CO2 permeance at fixed pore offset 2.1 nm. It is noted that the critical values of these four gases are different. With the smallest molecular size, the permeation of H2 is significantly faster than others and the critical value of interlayer distance is \( \approx 0.9 \text{ nm} \) in Fig. 2(b).

While the critical values of interlayer distance for CH4 and N2 are both 1.0 nm in Fig. 2(c) and (d). Higher critical value might be caused by the higher interaction with GO interlayer galleries. To confirm this speculation, we used RDF to characterize the affinity of GO [35] to gases. RDF is estimated:

\[
g_i(r) = \frac{N_i(r)V}{4\pi r^2 \Delta r N_j}
\]

where \( V \) is the cell volume, \( r \) refers to the distance between atom species \( j \) (gas molecules) and \( i \) (GO membranes atoms), \( N_i \) is the number of atom types \( j \), and \( N_j (r) \) is the number of species \( j \) within a shell from \( r \) to \( r + \Delta r \).

The \( g(r) \) of four pure gases around the oxygen function groups are shown in Fig. 4, taking the GO membrane with 0.9 nm interlayer distance and 0.0 nm pore offset as a representative. The affinity of GO membranes for the four gases decreases with the order of CO2 > N2 ≈ CH4 > H2. Stronger affinity with GO membrane makes gas molecules stay longer in interlayer gallery. Among these gases, CO2 is the most significantly affected by interlayer distance and pore offset, so that its critical value is the highest one, although its molecular size is smaller than N2 and CH4.

### 3.2. Mixed gas H2/CO2 separation

Oxygen functional groups in GO membranes provide CO2 gas preferential adsorption, which can be used to separate CO2 from mixed gas H2/CO2. In H2/CO2 separation through GO membrane process, the dominant factor, sieving effect or preferential adsorption, depends on interlayer distance and pore offset. The selectivity was calculated by

\[
s_A = \left( \frac{x_A^{SL}}{x_A^{PL}} \right) \left( \frac{x_A^{SL}}{x_A^{PL}} \right)
\]

where \( x_A^{SL} \) and \( x_A^{PL} \) are the mole fractions of the components A and B in feed side, and \( y_A^{SL} \) and \( y_A^{PL} \) are their mole fractions of in permeated side. As shown in Fig. 5(a), reverse selectivity for H2/CO2 separation, namely CO2-selective and H2-selective, which are respectively governed by preferential adsorption and sieving effect, were found as varying the interlayer distance and pore offset of the GO membrane.

CO2 adsorption amount on GO surface with 0.5 nm width according to \( g(r) \) results is presented in Fig. 5(b). When GO membrane has a narrow interlayer distance (\( D = 0.8 \text{ nm} \) and 0.9 nm), it tends to separate CO2 preferentially. With pore offset elongating, the decrease of CO2...
preferential adsorption amount results in lower CO$_2$ permeation but higher H$_2$/CO$_2$ selectivity. Density analysis of mixed gas H$_2$/CO$_2$ in last 5 ns in Fig. S4 shows that the peaks of CO$_2$ adjacent to dotted lines is larger than that of H$_2$, which suggests that the upper surfaces are preferentially occupied by CO$_2$ molecules rather than H$_2$ due to higher affinity with GO membrane. CO$_2$ adsorption amount decreases with pore offset, and then most of them enter into interlayer gallery, shown in Fig. S4(a). In these sufficiently narrow interlayer galleries, only one CO$_2$ layer is accommodated in interlayer gallery, indicated by the only one peak appearing between two dotted lines in Fig. S4(a). This cramped CO$_2$ takes up the whole transport space so more energy barrier is generated for latter H$_2$ entering into. In this case, the preferential adsorption effect prompts GO to selectively permeate CO$_2$. Kim and Yoon revealed that highly interlocked GO membranes which have a narrow transport interlayer gallery exhibited a highly CO$_2$ permeable character [5,34], which is ascertained by our simulation. The Video 1 of mixed gas H$_2$/CO$_2$ permeation through GO membrane with 0.8 nm interlayer distance and 0.0 nm pore offset is provided in supplementary to support this conclusion.

However, wider interlayer galleries with 1.2 nm or 1.4 nm interlayer distances accommodate more than one layer of CO$_2$ molecules. The bulk behavior makes the maximum carrying capacity and diffusion of CO$_2$ molecules that accommodated in interlayers independent with the pore offset in Fig. 3, which results in the adsorption amount of CO$_2$ on GO surface independent with pore offset in Fig. 5(b). The Video 2 of mixed gas H$_2$/CO$_2$ permeation through GO membrane with 1.2 nm interlayer distance and 0.0 nm pore offset is provided in supplementary. CO$_2$ sorption amount is relatively modest and most of them move away from the entrance and make room for H$_2$ entering. With smallest molecular size and weaker affinity with GO membrane, H$_2$ permeate promptly through the downstream layer by trajectory analysis shown in Fig. 6(a). Stronger affinity leads CO$_2$ stay longer in GO membranes shown in Fig. 6(b). In these cases, the preferential adsorption retards CO$_2$ permeation and sieving effect promotes H$_2$ permeation. Experimental study also found that an annealed GO membrane with additionally permeation pathways can achieve excellent H$_2$ selective permeation for H$_2$/CO$_2$ mixture [35]. These membranes had more

Fig. 5. (a) Mixed gas selectivity of H$_2$ and CO$_2$ with a variable of pore offset and interlayer distance. Solid lines and dotted lines represent the cases of CO$_2$ and H$_2$ preferential selected, respectively. Four representative interlayer distances are represented by different colors. D = 0.8 nm (black), D = 0.9 nm (red), D = 1.2 nm (blue) and D = 1.4 nm (purple); (b) CO$_2$ adsorption amount on GO surface with a variable interlayer distance and pore offset. Different interlayer distances (D) are represented by four colors. (D = 0.8 (black), 0.9 (red), 1.2 (blue), and 1.4 (purple)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Video 1.
channels for gases to rapidly permeate. Thus, with a large free transport interlayer space, GO membrane shows preferential permeation of H$_2$ over CO$_2$ and molecular sieving dominates the overall transport. Furthermore, higher H$_2$ selectivity was achieved through smaller sized pores, as shown in Table S1. This work focused on the qualitative mechanism understanding of the reverse selectivity for H$_2$/CO$_2$ se-

Video 2.

Fig. 6. Trajectories of randomly selected molecules (represented by different colors) for H$_2$/CO$_2$ separation through double-layer GO membranes with 1.2 nm interlayer distance and 0.0 nm pore offset. (a) H$_2$ trajectories; (b) CO$_2$ trajectories. GO sheets are located at two dotted lines.

Fig. 7. (a) Schematic mechanism for H$_2$/CO$_2$ gas mixture separation through a GO membrane with 1.2 nm interlayer distance and 2.1 nm pore offset; (b) The image of CO$_2$ preferentially adsorbed on GO surface; (c) The image of gas transport in wilder interlayer gallery.
paration. The schematic mechanism is shown in Fig. 7. With a higher affinity to oxygen-containing functional groups grafted on GO surface, CO₂ molecules are preferentially adsorbed on GO surface. These adsorbed CO₂ molecules occupy the pore space, as shown in Fig. 7(b), which becomes an obstacle to H₂ permeation. For the GO membrane with 1.2 nm interlayer distance and 2.1 nm pore offset, the above adsorbed CO₂ can shift away from the entrance to other interlayer galleries. Thus H₂ molecules can easily enter in the membrane. Thanks to its smaller molecular size and weaker interaction with GO, H₂ molecules can permeate promptly through the downstream layer. On the contrary, CO₂ molecules will be trapped for a long time. As a result, the observed number of permeated H₂ molecules at the vacuum side is more than CO₂ in Fig. 7(a).

4. Conclusions

MD simulation was performed to provide a molecular insight into the permeation behavior of pure gases (H₂, CH₄, N₂ and CO₂) and gas mixtures (H₂/CO₂) through double-layer GO membranes. The permeation performance is sensitive to interlayer distance and pore offset. Gas permeation was enhanced by increasing interlayer distance and pore offset till bulk behavior occurs. For H₂/CO₂ mixtures, a reverse selectivity was observed as increasing the interlayer distance and pore offset. Permeation through narrower interlayer gallery, CO₂ was preferentially adsorbed on GO surface to lead its selective permeation over H₂. Larger interlayer gallery favors H₂ selective permeation due to the dominant separation mechanism is replaced by sieving effect. H₂/CO₂ selectivity was increased with pore offset and interlayer distance. This simulation gives an atomic insight into gas permeation behavior of layered GO membranes and might contribute to understand the separation mechanism of GO membranes.

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