Graphene oxide membranes with high permeability and selectivity for **dehumidification of air**

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Abstract

Hierarchically stacked 2D graphene oxide (GO) membranes are a fascinating and promising new class of materials with the potential for radically improved water vapor/gas separation with excellent selectivity and high permeability. This paper details dehumidification results from flowing gas mixtures through free-standing GO membrane samples prepared by a casting method. The first demonstrated use of free-standing GO membranes for water vapor separation reveals outstanding water vapor permeability and H₂O/N₂ selectivity. Free-standing GO membranes exhibit extremely high water vapor permeability of 1.82×10^5 Barrer and a water vapor permeance of 1.01×10^{-5} mol/m²sPa, while the nitrogen permeability was below the system's detection limit, yielding a selectivity $>10^4$ in 80% relative humidity (RH) air at 30.8 °C. The results show great potential for a range of energy conversion and environmental applications.

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1. Introduction

Dehumidification is an energy intensive and widely needed process in building air-conditioning [1], dehydration of natural gases [2,3], and moisture regulation as part of protective apparel [4]. For example, based on the 2010 U.S. Department of Energy (DOE) report, buildings consume 40% of the primary energy in the United States; space air-cooling accounts for about 12.7% of the total energy consumption and 13.0% of CO₂ emission from buildings [5]. The current building space cooling by vapor compression system has two main disadvantages: Energy consumption is high and the process is accompanied by water condensation from fresh humid air intake. Therefore, it is highly desirable to develop a novel airconditioning system that can efficiently control building temperature and humidity in warm and humid climates. Several new dehumidification technologies have been reported over the last two decades, including electro-osmotic dehumidification [6], solid adsorbents [7], and liquid dessicants [8,9]. However, these technologies have high capital costs and exhibit no significant decrease in energy consumption and have therefore not yet been widely adopted for buildings.

In this line of research many different polymer membrane materials have been investigated for the removal of water vapor from gas streams [10,11,12]. Water vapor/air separation is driven by a pressure gradient of water vapor between two sides of the membrane under a constant temperature. Membrane dehumidification is a green process during which no environmentally harmful emission is generated. Semi-permeable membrane materials are used to selectively remove water vapor from a humid air stream. The water vapor permeability and the corresponding H₂O/N₂ selectivity strongly depend on the materials used. Membrane materials like PEBAX[®] MV 1074¹ and sulfonated poly(ether ether ketone) (SPEEK) exhibit good performances. Commercially available PEBAX[®] MV 1074 combines a high water vapor

¹ <http://www.arkema.com/en/>

permeability of 1.6×10^5 Barrer with a medium $\text{H}_2\text{O}/\text{N}_2$ selectivity (2.0×10^5). SPEEK offers a lower water vapor permeability of 7.0×10^4 Barrer combined with an extremely high $\text{H}_2\text{O}/\text{N}_2$ selectivity (1.0×10^7) [3].

Graphene oxide (GO) sheets, which are oxidative exfoliation products of graphite, have attracted growing interest in areas of energy storage and separation technologies [13]. In particular, GO sheets, which contain carboxyl, hydroxyl, and epoxide functionalities in different ratios, offer great potential as material for functional composite membranes that have excellent water transport properties [14]. Unlike GO, if one uses pristine graphene monolayers, one has to create highly engineered pores in the sheets to allow permeation [15]. Despite increased academic interest in water transport through graphene and GO membranes significant technical difficulties still hinder the fabrication of such membranes for real-world water separation applications. For instance, it is still impractical to prepare large areas of monolayer graphene [13]. It is also extremely challenging to generate a high density of nanopores with controllable, relatively uniform pore sizes on graphene sheets [16].

Using stacked GO nanosheets instead of nanoporous graphene-based membranes, offers a more realistic approach to fabricating water vapor-selective membranes. The two dimensional (2D) channels between the stacked GO nanosheets allow water molecules to pass through while rejecting unwanted solutes, a mechanism similar to that of water transport through pores in traditional membrane structures. Molecular simulations have predicted that water has a very large slip length (i.e., low friction) on graphene surfaces, resulting in an extremely high rate of water flow in planar graphene nanochannels [17,18]. This property promises high water flux in stacked GO nanosheets as well. In addition, GO nanosheets can be mass-produced via chemical oxidization and ultrasonic exfoliation of graphite [19,20], thereby significantly lowering the

material manufacturing cost and facilitating scale-up of the membrane synthesis process. Furthermore, the functional groups (particularly carboxyl groups) on GO nanosheets provide convenient sites for further functionalization to enhance properties such as specific interactions with water contaminants [21]. Therefore, GO becomes an ideal material for fabricating high-performance membranes for water vapor separation. It has been demonstrated that membranes consisting of stacked GO nanosheets, made by a simple solution filtration method, exhibit excellent mechanical strength in dry conditions and can be used as a gas/vapor separation membrane. Superfast permeation of water vapor through such a GO membrane was observed and credited to a nearly frictionless flow of monolayered water through the planar capillaries formed by the closely stacked GO nanosheets [13].

In this paper, we report dehumidification results from flowing gas mixtures through free-standing GO membrane samples prepared by a casting method. This first demonstration of a GO membrane for water vapor separation shows outstanding water vapor permeability and H₂O/N₂ selectivity.

2. Experimental

2.1 GO synthesis and membrane preparation

Graphite flakes (Sigma-Aldrich, cat #332461, 150 μ m flakes) were oxidized using the method reported by Marcano *et al.* [19]. This “improved method” (with respect to Hummers’ method [22]) uses increasing the amount of KMnO₄ and a 9:1 mixture of H₂SO₄/H₃PO₄, excluding the NaNO₃ to improve the efficiency of the oxidation process. Details of the synthesis procedure are described in the supporting information. Subsequently an aqueous GO slurry, containing about 0.89 wt.% of flakes, was poured onto a polished Teflon plate. The slurry was

spread out with a glass bar. To achieve the desired film thickness, 5-10 layers of scotch tape (3M) were taped onto the Teflon plate acting as spacers. The sample was dried overnight, and then the film was lifted off using adhesive tape and careful peeling.

2.2 Membrane characterization (material)

X-ray diffraction (XRD) pattern of GO membranes were obtained on a Rigaku desktop X-ray diffractometer using Cu K α (1.54059 Å) radiation with the X-ray generator operating at 20 kV and 30 mA. Data were collected for a 2θ range of 5.0-20.0° at an angular resolution of 0.01 °/s. The morphology of GO membranes was studied by scanning electron microscopy (SEM) using a JEOL microscope model JSM5900LV. Membrane samples for SEM analysis were put on carbon sticky tape and plasma coated with Pt/Au for 240 s. Fourier Transform Infrared (FTIR) spectra were recorded over a range from 400-4000 cm⁻¹ with a resolution of 2.0 cm⁻¹, using a Nexus 670 FTIR spectrometer (Thermo Nicolet). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Quantera Scanning X-ray Microprobe (Physical Electronics). This system uses a focused monochromatic Al K α x-rays (1486.7 eV) source and a spherical section analyzer. The instrument has a 32 channel detector. The X-ray beam used was a 100 W, 100 μm diameter beam that was rastered over a 1.2 mm by 0.1 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector was at 45° off-normal. High energy resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d5/2 line, these conditions produced a FWHM of 0.91 eV. The binding energy (BE) scale is calibrated using the Cu 2p3/2 line at 932.62 ± 0.05 eV and Au 4f7/2 at 83.96 ± 0.05 eV for known high purity references.

2.3 Water vapor permeation test

Membrane permeation tests were carried out using the method reported by Liu *et. al.* in 2011 (see supporting information for details about the procedure) [23].

The permeation flux, permeance, and selectivity were calculated from experimental measurements according to the following equations:

$$J_m = \frac{W_p}{(SA_m)t}$$

$$P_i = \frac{F_{i,p}}{(SA_m)(\Delta p_i)}$$

$$S_{ij} = \frac{(y_i/y_j)_p}{(x_i/y_j)_f}$$

With J_m = permeation flux [kg/m²/h], P_i = permeance of species i [mol/m²/s/Pa], S_{ij} = separation factor of species i to j , W_p = amount of liquid condensed in the liquid N₂ trap, SA_m = working surface area of the membrane [m²], t = testing duration time to collect W_p [s], F_i = permeation flow rate of species i [mol/s], Δp_i = partial pressure differential of species i between the feed and permeate sides [Pa], y_i = molar fraction of species i on the permeate side, y_j = molar fraction of species j on the permeate side, x_i = molar fraction of species i on the feed side, and x_j = molar fraction of species j on the feed side.

3. Results and Discussion

3.1 Membrane characteristics

Materials characterization results of a typical GO membrane are summarized in Fig. 1. Fig. 1a shows a photograph of the free-standing, flexible GO membrane prepared by the described casting method. In the XRD pattern (Fig. 1b) the (001) peak of the GO membrane material is located at $2\theta = 11.18^\circ$ (d -spacing: 7.91 Å). None of the characteristic peaks of the graphite starting material (e.g. the 100% peak at $2\theta = 26.96^\circ$ (002) [24]; Fig. 1b inset) could be detected, which indicates that pure, highly oxidized GO was synthesized. High resolution XPS scans of the carbon region (C1s) were performed on a GO membrane. Deconvolution of the spectrum's C1s region revealed the presence of a strong peak at ~286.6 eV, corresponding to large amounts of sp^3 carbon (C-O), with contributions of C=C (~284.5 eV), C=O (~287.8 eV) and carboxyl (O-C=O)/lactone/ester (~288.9 eV) groups (Fig.1c). The high content of oxygen in the membrane material is due to the strongly oxidative exfoliation during the synthesis procedure. Table 1 lists the quantified atom percentage of carbon and oxygen found in the surface composition of GO membranes as determined by XPS. As shown Fig. 1d, thus prepared GO membranes exhibit significant surface roughness, most likely formed during the drying process (water evaporation on the PTFE plate). GO flakes coated on Si(100) surface are ave. 20-40 μm in their lateral dimension and they consist of 1-2 GO layers (Fig. 2).

Fig. 1. (a) Photograph of a typical GO membrane prepared via a casting process, (b) region of the XRD pattern, which contains the diffraction peak indicating the d -spacing between GO layers, and inset shows the graphite starting material and GO, (c) XPS (C1s region), and (d) SEM image of the GO membrane surface.

Table 1.

Physical properties of a free-standing GO membrane prepared by the improved method.

d -spacing ($\text{\AA}$)	Ave flake size (μm)	C/O ratio (at.%)	C1s (at.%)				Thickness (μm)
			$\text{C}=\text{C}$	$\text{C}-\text{O}$	$\text{C}=\text{O}$	$\text{C}(\text{O})-\text{O}$	
7.91	20-40	54.6/45.4	26.3	62.4	8.8	2.4	6.0

Fig. 2. (a) Scanning electron microscope (SEM) and (b) atomic force microscope images of GO flakes including a height profile of the GO flake.

Fig. 3 shows the FTIR spectrum of a GO membrane. The GO membrane shows a strong broad feature of overlapping vibration modes between $3600\text{--}2800\text{ cm}^{-1}$, which can be attributed to water clusters associated with O-H groups on the membrane surface. Other identifiable vibration modes are C=O (1732 cm^{-1}), aromatic C=C (1611 cm^{-1}), carboxy C-O (1410 cm^{-1}), epoxy C-O (1226 cm^{-1}), and alkoxy C-O stretches (1051 cm^{-1}) [25].

Fig. 3. FTIR spectrum of a GO membrane

3.2 Gas and water vapor permeation

To investigate the potential of GO membranes for dehumidification, the single gas permeability for nitrogen and oxygen was measured. In addition, the mixed nitrogen and water vapor permeability of the same GO membrane was also assessed. The permeation results for a single gas (N₂, O₂) and gas mixtures (N₂ plus H₂O) through GO membranes are summarized in Table 2. GO membranes show very low permeance for pure gases (N₂, O₂) in the absence of water vapor. The oxygen permeability is slightly higher than that of nitrogen, and both permeabilities decrease as the cell temperature increases. This observation is surprisingly different from the behavior of polymer membranes, where gas permeabilities are enhanced at higher operation temperatures due to the swelling of the polymer [3]. This might be due to decrease of the interlayer spacing of GO membranes as the temperature increases [14, 26].

Table 2

Gas permeation results for GO membranes at different mole fraction of water and different cell temperatures, respectively.

Component		Permeability (Barrer*)/Permeance (mol/(m ² s Pa))			
<i>Single gas</i>					
Cell temperature (°C)	29.1	31.0	31.2	31.5	
N ₂	147/8.33 x 10 ⁻⁹	103/ 5.76 x 10 ⁻¹⁰	0.00	0.00	
O ₂	491/2.74 x 10 ⁻⁸	248/1.44 x 10 ⁻⁸	107/6.19 x 10 ⁻⁹	107/6.19 x 10 ⁻⁹	
<i>Mixed feed (H₂O mole fraction: 0.02)</i>					
Cell temperature (°C)	22.5	30.8	43.4		
N ₂	0.00	0.00	98 / 16		
H ₂ O	1.82 x 10 ⁵ /1.01 x 10 ⁻⁵	1.82 x 10 ⁵ /1.01 x 10 ⁻⁵	8.78 x 10 ⁴ /4.95 x 10 ⁻⁶		
<i>Mixed feed (H₂O mole fraction: 0.033)</i>					
Cell temperature (°C)		30.0	43.2		
N ₂		0.00	0.00		
H ₂ O		1.70 x 10 ⁵ /8.62 x 10 ⁻⁶	1.19 x 10 ⁵ /6.58 x 10 ⁻⁶		
<i>Mixed Feed (H₂O mole fraction: 0.065)</i>					
Cell temperature (°C)			43.4		
N ₂			0.00		
H ₂ O			8.03 x 10 ⁴ /4.50 x 10 ⁻⁶		

* 1 Barrer = 3.348 x 10⁻¹⁶ mol m/(m² s Pa)

The permeation of water molecules across the membrane, however, is driven by a partial pressure gradient of water vapor in the $\text{H}_2\text{O}/\text{N}_2$ gas feed, so that the water vapor flux becomes higher with increasing water content in the gas feed, i.e. higher mole fractions of water (humidity). Fig. 4a shows the water flux through GO membranes as a function of the test cell temperature for different mole fractions of water vapor: 0.014, 0.02, 0.033 and 0.065. As expected the water flux increases with increasing mole fractions of water, but more interestingly, the water flux seems to decrease with increasing cell temperature. as Nair *et. al.* suggested permeation may occur by slip-free flow of liquid like water between the layers [14]. Therefore, as cell temperature increases the amount of water decreases in the gallery spaces by the partitioning of water between liquid and vapor phase, this could reduce permeability. The influence of the test cell temperature on the water vapor permeance of GO membranes follows the same trend and is shown in Fig. S1 (see supporting information). It decreases with increasing test cell temperatures.

Fig. 4. Variation of (a) water flux through GO membranes as a function of the test cell temperature for different mole fractions of water vapor, and (b) water vapor permeance of GO membranes as a function of water mole fraction in feed gas at different operating cell temperature.

The presence of water vapor in the gas feed mixture significantly influences the gas permeability of GO membranes. Usually, gas permeabilities in **polymer** membranes are higher for the wet state of a membrane than for the dry state **due** to their swelling [3]. However, in the GO membranes N_2 gas permeabilities remain below the detection limit of our system compared to the exceptional water vapor permeability (up to 1.82×10^5 Barrer), even as the water vapor permeability of the GO membranes decreases slightly with increasing cell temperatures. This indicates that GO materials are much more stable and less sensitive to temperature variations than polymer materials in the presence of water vapor at temperature ≤ 40 °C. However, at temperatures higher than 40 °C the GO surface becomes less hydrophilic, which leads to decreased water vapor permeability and detectable N_2 permeability at lower mole fractions of water (e.g. 0.02) [27]. Overall, our data indicates that the selectivity of water vapor to N_2 gas is exceptionally high for GO membranes, which are basically impermeable to N_2 gas. The water vapor permeability and selectivity over N_2 gas are comparable to commercially available polymer membranes, such as PEBAX® MV 1074 (water vapor permeability = 1.6×10^5 Barrer, selectivity = 2.0×10^5) [12].

Fig. 4b shows the water vapor permeance of GO membranes as a function of humidity, i.e. mole fraction of water vapor in the feed gas, at different test cell temperature in a N_2/H_2O gas feed mixture. In all cases the N_2 permeance is close to lower detection limit of the instrument at the same time (Table 2). The water vapor permeance is higher at lower test cell temperatures, and remains rather steady for different mole fractions of water, i.e. different humidities. As

mentioned above, this leads to very large H₂O/N₂ selectivities for GO membranes under the various test conditions, with the exception of one condition we explored: at a low humidity (0.02 mole fraction of water) and high temperature (43.4 °C) the H₂O/N₂ selectivity was found to decrease to ~816 (down from infinity at higher humidity or at lower temperature, Table 2). As discussed earlier, this might be resulted from the decreased amount of water in the interlayer spacing at the temperature, and this could dramatically decrease permeability [14]. However, even under this condition GO membranes still exhibit excellent barrier behavior with respect to nitrogen. Unfortunately, the humidity and temperature ranges on the water vapor permeance of GO membranes are limited. Excessive water vapor adsorption at higher test cell temperatures and/or humidities leads to mechanical failure of the GO membrane and leakage is observed.

In the water vapor permeation test cell GO membranes were continuously measured for 4 days under humid conditions. After removal from the test cell no structural degradation of the GO membranes were observable, but both membrane surfaces were covered with substantial amounts of condensed water vapor. One of the GO membranes was investigated by XRD right after the water vapor permeation test and then again after drying it in air for 30 d (XRD recorded on the side of the membrane facing the feed gas stream, Fig. 5). The XRD pattern of the wet GO membrane after testing showed a large expansion of the *d*-spacing (11.40 Å) compared to the *d*-spacing of an as-prepared membrane (7.91 Å). The intensity of the peak was dramatically decreased and exhibited a slightly deformed pattern. However, after drying for 30 d in air *d*-spacing decreased again to 7.62 Å, almost recovering to its original value.

Fig. 5. XRD pattern of an as-prepared GO membrane (black), a GO membrane right after a water vapor permeation test (blue), and the same membrane after being dried in air for 30 d (red).

3.3 Comparison of GO membrane water separation performance

Water vapor permeabilities and selectivities of H₂O/N₂ of several membrane materials that are being used or investigated for dehumidification applications are listed in Table 2 and compared with the properties of our GO membranes. For convenience membrane permeability and permeance are listed separately in Barrer and mol/(m²sPa), respectively. At low humidity (0.02 mole fraction H₂O) and temperature (≤ 40 °C) the GO membranes prepared in this work exhibit outstanding water vapor permeability of 1.82×10^5 Barrer and permeance of 1.01×10^{-5} mol/(m² s Pa), which is superior to most values documented in Table 2, including those for all polymer membranes. It is similar to the permeability reported for [emim][Tf₂N], an ionic liquid. For a NaA zeolite/Ni sheet membrane a significantly higher water vapor permeability of 6.09×10^4 Barrer has been reported, but this membrane exhibits a low selectivity for H₂O/N₂ gas mixtures (178). Regarding the H₂O/N₂ selectivity, values as high as 1.0×10^7 were reported for SPEEK and PEBAX® MV 1074 polymers. Other membranes, including polyethylene glycol and [emim][Tf₂N], showed H₂O/N₂ selectivities above 2000. Unfortunately, those selectivity

numbers were mostly measured using single gas experiments and therefore do not represent actual separation factors of a gas mixture. On the other hand, our GO membranes exhibit excellent H₂O/N₂ selectivity $>10^4$ in a H₂O/N₂ gas mixture. This number is clearly better than those of other membranes in gas mixtures.

Table 2
Membrane materials used for air defumidification.

Membrane material	Water vapor permeability, Barrer	Water vapor permeance, mol/(m ² s Pa)	H ₂ O/N ₂ selectivity	Reference
Sulfonated poly(ether ether ketone) (SPEEK)	7.00×10^4	4.60×10^{-7}	1.0×10^7 *	[3, 28]
PEBAX [®] MV 1074	1.60×10^5	2.87×10^{-6}	2.0×10^5 *	[3]
Ionic liquid [emim][Tf2N]	2.83×10^5	2.10×10^{-7}	3843*	[28]
Stabilized liquid poly ethylene glycol	1.50×10^4	7.50×10^{-7}	2000*	[29]
NaA zeolite/Ni sheet	6.09×10^4	6.8×10^{-6}	178	[30]
Graphene oxide	1.82×10^5	1.01×10^{-5}	$>10^4$	this work

*The selectivity was calculated as a ratio of relative permeability of single gas.

This comparison against other materials for dehumidification membranes is encouraging.

However, currently there are a couple of limitations to the use of GO membranes for dehumidification. First, as previously mentioned, GO membranes showed decreased water vapor/N₂ selectivity as the separation temperature increased. Second, GO membranes can be recycled, but currently it is a slow process to do so. Third, GO membranes used in this study are too fragile to be used in any system with cross-membrane pressures >2 bar, which makes this generation of GO membranes not suitable for the treatment of natural gases, where operating pressure differentials could be greater than 12 bar [31]. On the other hand, GO membranes could

be competitive for lower pressure gas separation systems such as flue gas dehydration and building ventilation systems [3].

4. Conclusions

We have demonstrated that GO membranes with excellent water vapor permeability and H₂O/N₂ selectivity can be synthesized via a simple casting approach. The GO membranes exhibit a number of fascinating advantages over existing membranes: first, graphite is an inexpensive raw material, which significantly lowers the membrane fabrication cost; second, the synthesis procedures for both GO nanosheets and GO membranes are simple and scalable; third, water vapor permeability through GO membranes dominates the permeability of other gases such as O₂ and N₂, leading to exceptional selectivities. Further adjusting the properties of the GO starting material, such as flake size, surface functionalization or incorporating a support material to increase mechanical stability, is expected to yield enhanced performances with regard to water vapor flux and salt rejection.

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