Swelling Pressures of Graphite Oxide and Graphene Oxide Membranes in Water and Ethanol

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Swelling of graphene oxide (GO) membranes and bulk graphite oxide under confinement conditions is found to produce pressures up to \( \approx \) 220 bar. Swelling pressure is important to take into account in many applications of GO membranes, but it has not been previously reported. Swelling pressures are typically measured only for bulk materials. However, it is demonstrated that even \( \mu \)m thick GO membranes develop pressures 3–25 bar due to the volume expansion caused by swelling in water. A rather strong difference in kinetics of pressure increase is found for both graphite oxide and GO membranes in water and ethanol despite similar lattice expansion due to swelling. This effect is attributed to slower penetration of ethanol into GO interlayers. Significantly faster saturation of swelling pressure is found for GO membranes (few hours) as compared to bulk graphite oxides (weeks) due to a higher degree of compaction. Swelling pressure is an important factor in applications, which require confinement, encapsulation of GO membranes or using external pressure to limit the lattice expansion. Finally, the swelling pressure can be used as an estimation for the suction pressure developed in pervaporation or vapor permeation applications, which is suggested as a driving force in rapid water permeation across GO membranes.

1. Introduction

Multilayered graphene oxide (GO) laminates in the form of papers,[1] thin films,[2] or membranes[3–5] attracted a lot of attention over the past few years. The membranes were proposed for many applications, e.g., for gas separation,[6] nanofiltration,[7–9] concentration of salts in solution,[43] temperature[44] etc., which depends on many parameters, e.g., degree of compaction, separation of solvent mixtures,[10,11] as a toxicant barrier[12] and water desalination.[13] Graphite oxides are used as precursors to prepare dispersions of GO in water or other polar solvents.[7,14] Drop casting,[8] spin coating,[15] and vacuum filtration[16,17] are the methods commonly used for the preparation of GO thin films and freestanding foils/membranes.

Most of the applications cited above are enabled by the ability of GO multilayers to swell in polar solvents similarly to their precursor graphite oxides.[18–22] In this respect GO is similar to very common clay minerals, e.g., montmorillonites,[23] vermiculites,[24] and bentonites.[25] Swelling occurs in these materials due to sorption of water (or other solvents) between 2D layers and the expansion of interlayered distance.[26–28] The driving force of swelling is hydration of anions in clay minerals and hydration of interlayer functional groups in GO. The crystalline swelling refers to layer-by-layer intercalation of solvent. Osmotic swelling is controlled by the relatively easy flow of solvent in and out of structure regulated by osmotic effects.[29–33] Remarkably, crystalline swelling is found for Brodie GO in all so far studied solvents except water[34–38] while for Hummers GO only osmotic-like swelling was so far reported.[37,39,40]

Adding water to clays under conditions of confinement is known to produce pressures in the range of tens or even hundreds of bar.[23,41,42] Swelling pressure is complex phenomena, which depends on many parameters, e.g., degree of compaction,[29] concentration of salts in solution,[43] temperature[44] etc., It is an important factor, e.g., in construction works since the pressure is sufficient to induce damage in buildings or roads. Swelling pressure has been studied in detail for clay minerals but so far not reported for multilayered GO and graphite oxides. At the same time, the swelling pressure is an important factor affecting performance of GO membranes.

The swelling of GO membranes is directly related to the size of “permeation channels” which enable a flow of solvents and solutions. Strong variation in the size of the “permeation channels” is observed in GO membranes depending on the solvent used,[45] concentration and chemical nature of dissolved molecules or ions,[15] shelf storage time,[46] and many other parameters related to the preparation of membranes. For example, the swelling in liquid ethanol was reported with significant scatter providing d(001) values in the range \( \approx \) 11–17 Å.[40,46,47] Swelling in longer alcohols provides interlayer distances up to \( \approx 50 \) Å.[40,48] There are also examples showing that the swelling of GO membranes can be significantly different compared to precursor graphite oxides.[16,17]

Strong variation of interlayer distance in swollen GO membranes is a problem for nanofiltration applications, which require...
precise control of permeation channel size. Several methods were proposed to control or modify the interlayer distance of GO membranes, e.g., using crosslinking of GO planes or intercalation of certain molecules or ions and encapsulation in hardened glue. The idea of using glue encapsulation is to preserve the swelling typical for different humidity conditions at the conditions of immersion of the membrane in liquid water. However, the effects of swelling pressure were not taken into account in this and several other studies where external pressure was proposed as a method to control interlayer distance of GO laminates. It is clear that expansion of GO structure cannot be prevented by the external pressure smaller than swelling pressure developed by material.

Moreover, the effects of swelling pressure are likely to be relevant to a discussion of driving force in vapor permeation of GO membranes. The exact mechanism of water (and other solvents) flow inside of the GO interlayers was a subject of significant debate over the past few years. Several studies postulated the existence of “capillary-like” pressure on the scale of hundred bars as a driving force in GO membrane pervaporation following experimental observation of high flux of pure water across GO membranes. However, using the macroscopic concept of capillary forces is not a valid approach for nanometer-sized interlayers.

In this study, we report for the first time measurements of swelling pressure in compacted graphite oxide and GO membranes. Experiments with compacted graphite oxide powders demonstrate swelling pressure exceeding 200 bar in water and ethanol. Multilayered GO membranes develop pressure in the direction normal to the planar surface in the range 1–25 bar depending on the membrane thickness. It is demonstrated that swelling pressure needs to be taken into account in several applications of GO multilayers, while hydration provides a pressure gradient for vapor permeation across GO membranes.

2. Results

2.1. Swelling Pressure Measurements with Powder Graphite Oxide

Figure 1. Schematic idealized representation of swelling pressure tests performed: a) using graphite oxide samples (grains with random orientation) and b) using GO membranes (flakes mostly aligned parallel to the bottom of cell). Water (or ethanol) is provided through the small hole in the piston under 0.3 bar pressure, the suction of water into the sample results in swelling pressure measured in a direction normal to the GO membrane plane. Faster equilibration is achieved in smaller samples. As expected, the swelling pressure was found to increase rather slowly in experiments with bulk graphite oxide powder samples.

Figure 2 shows that the maximal pressure of 226 bar was achieved for graphite oxide in water. Graphite oxide in ethanol has rather minor contribution to the overall swelling pressure. The swelling pressure tests performed in our study include experiments with standard bulk powder samples and samples of freestanding GO membranes with a thickness of tens of micrometers. Thin membrane samples were never previously tested for swelling pressure to the best of our knowledge. That is not only for GO but also for other types of swelling membranes. The intracrystalline swelling originates from an expansion of GO lattice caused by intercalation of water or ethanol. The orientation of graphite oxide grains in a bulk sample is random at the moment of loading except for some preferential orientation due to uniaxial compaction. The powder sample also unavoidably includes some voids between the individual grains (Figure 1a). In contrast, the GO membrane has 2D flakes well-aligned parallel to each other, essentially forming a strongly disordered single crystal composed by densely packed GO lamellae. The swelling of GO membrane structure results in the lattice expansion normal to the membrane plane and directly measured using the load cell (Figure 1b). According to X-ray diffraction (XRD) the only detected change in GO structure due to swelling is an increase of interlayer distance. However, some swelling in interplane direction of membranes is also possible, e.g., due to flattening of wrinkles and slight increase of spaces between flakes along the planes. However, we believe that this part of swelling has rather minor contribution to the overall swelling pressure.

As shown in Figure 1, the diffusion pathway of solvent is different in powder and membrane samples. A significant part of the solvent diffusion pathway goes around grains of graphite oxide through voids, while in the case of GO membranes most of the solvent is directly sucked into the interlayers and propagates along the disordered lattice. The pressure increase rate is limited by the diffusion of solvent provided through the hole in the stamp.

Typically, the 10 g powder graphite oxide sample was loaded into the assemblage, water or ethanol supplied under conditions of sample confinement and pressure measured as a function of time (Figure 2). The pressure inside of the cell increased slowly with full equilibration achieved after 3–4 weeks. Equilibration is achieved when the sample is saturated by solvent. Figure 2 shows that the maximal pressure of 226 bar was achieved for graphite oxide in water. Graphite oxide in ethanol...
exhibited maximal pressure of 194 bar, but equilibration was not achieved even after 35 days.

It is interesting to note that swelling of graphite oxide in ethanol results in a stronger expansion of GO structure revealed by XRD as an increase in d(001) value (Figure 3). The d(001) value increases up to 16.3 Å in liquid ethanol and up to 13.4 Å in liquid water providing stronger volume increase for swelling in ethanol. The swelling of freshly prepared GO membranes in water and ethanol is very similar to swelling of graphite oxides, according to our previous study.[40] Therefore, higher swelling pressure for GO in ethanol could be expected in our experiments compared to the bulk powder samples since the vacuum filtration becomes progressively slower with an increase of membrane thickness until it completely stops.

The slow increase of pressure measured in bulk powder samples is likely related to diffusion of water or ethanol between grains of graphite oxide (Figure 1). In contrast, it is known that the intracrystalline swelling occurs rapidly. For example, saturated swelling of graphite oxide immersed in liquid water is detected by XRD within the 1–2 min required for sample mounting and data recording.[55,56] It is known that highly compacted samples with smaller space between material’s grain exhibit higher swelling pressure and faster pressure increase in the standard tests.[43,57,58] Therefore, the obvious difference in the swelling pressure increase rate (Figure 2) can be assigned to slower diffusion of ethanol in graphite oxide powder sample.

2.2. Swelling Pressure Experiments with GO Membrane Samples

Most of the applications proposed for multilayered GO materials and GO membranes involve swelling in water or other polar solvents. However, swelling pressure effects were not yet evaluated or taken into account. The experiments presented below demonstrate that significant pressure is developed in confined GO membranes with thickness in the range of tens μm (~30–115 μm). It is challenging to prepare thicker GO membranes since the vacuum filtration becomes progressively slower with an increase of membrane thickness until it completely stops.

The results of GO membrane swelling tests are summarized in Figure 4. The increase of swelling pressure occurs significantly faster in GO membranes compared to the bulk powder samples. The final pressure also appeared to be strongly
dependent on the thickness of GO membranes. The swelling pressure of GO membranes increased in a sharp step within 0.5–1 h after adding water with saturation achieved within 3 h. The GO membrane can be considered as extremely poorly ordered single crystal with an orientation of layers parallel to the piston (Figure 1a). The data shown in Figure 4 also reveal that the thicker GO membranes tend to exhibit higher swelling pressure. The highest pressure of 22.7 bar (over the initial load pressure of 4.8 bar) was measured for 115 μm thick membrane in water. Some sample-to-sample variations within this trend can be explained by a difference in the membrane shape, density and mounting. For example, some cracks might appear in the process of initial loading of the membrane samples into the swelling pressure cell, thus increasing void volume.

The correlation between swelling pressure in water and thickness of GO membranes is shown in Figure 5. If the correlation is valid for thinner membranes, swelling pressures below 1 bar it could be expected for membranes with thickness <5 μm. However, measurements of swelling pressure for this thickness-pressure range require different type of experimental setup.

As noted above, it is not possible to prepare very thick GO membranes and certainly not possible to prepare membranes with a thickness comparable to the size of bulk powder samples described above. Therefore, we performed an additional experiment with small amount of graphite oxide powder as a reference.

The value of swelling pressure measured using standard cells and bulk powder samples (e.g., clays) is known to depend on the height for samples with the same diameter. The standard soil tests are typically performed with the diameter to height ratio of about 2.5. Significant decrease in swelling pressure was reported for smaller sample heights, but the change seemed to be rather specific for different materials.[59] This effect was also verified in our experiments with smaller loading of powder samples. The experiment with ~0.5 g powder sample developed swelling pressure 24.4 bar with saturation achieved after ~24 h (Figure S5, Supporting Information). This pressure is similar to the pressure developed by three times smaller (~150 mg) GO membrane.

A faster increase of swelling pressure in GO membranes (compared to powders) is explained by much smaller thickness of the membrane. It is also related to more rapid penetration of solvent in GO lattice. The continuous structure of GO membrane sample can be considered as one larger disordered crystal. The solvent can be sucked by this crystal and flow mostly through the GO interlayers unlike the powder samples where diffusion between individual grains is the limiting factor.

It is important to note that bulk density of the compressed powder is almost the same as bulk density of GO membranes. The density of GO membrane samples was estimated using the known diameter, thickness, and weight providing the value of 0.75–1.1 g cm⁻³ measured at ambient conditions. Despite the seemingly dense stacking of 2D layers in GO membranes, the bulk density is significantly lower than the real density of GO (~2 g cm⁻³). The difference between the real density of graphite oxide and the measured density of GO membranes demonstrates the presence of voids with a volume of 50%. The reason for the appearance of voids is likely related to the specifics of membrane synthesis. The GO membranes are produced by vacuum filtration of water dispersions at the condition of saturated water swelling. Drying the membranes results in ~50% decrease of volume due to decrease of interlayer distance in GO structure from ~13.5 to ~7 Å (under vacuum). Therefore, the voids can be formed between lamellae’s of GO sheets due to the water evaporation as lenses or spaces inside of wrinkles. The wrinkled lamellas and voids are typically clearly visible in
scanning electron microscopy images taken from the edges of GO membranes.\textsuperscript{[90,60]} Therefore, it can be anticipated that membranes specially compacted to decrease the volume of voids and to align GO flakes (as, e.g., in Refs.[11,61]) could exhibit even higher swelling pressure significantly exceeding 25 bar.

The swelling pressure of GO membranes in ethanol is found to increase significantly slower than in water, similarly to experiments with bulk graphite oxide. Figure 4 shows a slow increase of pressure after adding ethanol to the pressure cell. The swelling pressure measured for all membrane samples has not achieved saturation values after 20 h. Two experiments with swelling of GO membranes in ethanol were performed over the time extended to 120 h but even in this case saturation was not achieved. For example, 115 \(\mu\)m thick membrane showed an increase of swelling pressure from 4.8 bar after 20 h up to 9.7 bar after 140 h (Figure S6, Supporting Information).

A slow increase of swelling pressure for GO in ethanol is in agreement with earlier reported properties of GO membranes which demonstrated significantly faster water diffusion compared to ethanol.\textsuperscript{[5,10]} Slower increase of swelling pressure in ethanol is also in agreement with faster sorption of water from water/ethanol binary vapor mixtures.\textsuperscript{[15]}

3. Discussion

The swelling pressure measured on membranes is smaller compared to the powder samples, but anyway rather significant and needs to be taken into account in many application-related situations. Whenever the membrane is confined and exposed to liquid solvent or moisture, it will develop a pressure, in some cases tens and may be even hundreds of bar. Experiments also reveal that the magnitude and kinetics of swelling pressure is different depending on solvent.

Encapsulation of GO membranes, papers, and thin films in solid and plastic enveloping materials was reported in many studies.\textsuperscript{[13,62–64]} For example, the membranes are often fixed using metallic rings for permeation tests.\textsuperscript{[53]} Once the membrane is exposed to water or other polar solvents, it will develop pressure under the fixing rings or screws. The swelling pressure is also important, for example, in experiments with permeation of solutions along the plane of GO membranes, which requires encapsulation of flat surfaces of the sample in some glue (e.g., polydimethylsiloxane).\textsuperscript{[65]}

The structure of encapsulated membrane and the size of “permeation channels” will depend on the balance between external pressure and swelling pressure developed by the GO multilayers in liquid water (or other solvent/solution). It will also depend on the type of encapsulation: rigid versus elastic. For example, the thickness of perfectly stacked GO membrane increases by about 50\% due to swelling in water. That is due to the change of interlayer distance from \(\approx7.5\) Å at ambient humidity to \(\approx13.5\) Å in liquid water. The membrane will not expand inside of completely rigid encapsulation cell but develop significant pressure. However, if the encapsulation is elastic, the swelling pressure developed by the GO membrane will result in expansion of encapsulated volume, low pressure inside of encapsulated volume and interlayer distance similar to the encapsulation free conditions.

Therefore, swelling pressure is one of the key parameters to take into account in attempts to use external pressure or glue encapsulation to control interlayer distance of multilayered GO membranes.\textsuperscript{[64]} For example, the study by Abraham et al.\textsuperscript{[64]} was aimed to limit swelling of \(\approx100\) \(\mu\)m tick GO membranes in liquid water by enveloping it with epoxy glue. The study postulated that the GO lattice expansion is prevented by the glue. However, in situ characterization of structural changes for the encapsulated membrane was not presented. Our results demonstrate that the rigidly encapsulated membrane can develop significant pressure (over 20 bar) when exposed to liquid water. Therefore, the swelling pressure can be sufficient to completely prevent limiting effects of the encapsulation if the epoxy glue is elastic or not pressure resistant.

It is clear that the external pressure applied to the membrane must be higher than the swelling pressure developed by the membrane in liquid solution in order to induce expected limiting effects. Uniaxial external pressure on the level above 20 bar is likely to be sufficient to modify the structure of GO multilayers but possibly not to the full expected extent. It can be predicted that the effects of swelling pressure will be important in processes and operations with GO membranes, which occur at pressures below \(\approx20\) bar, for example in some pressure driven filtration experiments.\textsuperscript{[66,67]} It should be noted that the swelling pressure of GO was measured here only in pure water and ethanol. Using solutions of various salts can be expected to result in significantly different values of swelling pressure. The nature of dissolved ions, pH, and concentration of solutes are parameters which are known to affect swelling pressure in clays.\textsuperscript{[68–70]}

Swelling pressure developed by the exposure of GO to conditions of varying humidity or periodic immersion into liquids is also likely to affect the mechanical stability of composite materials. For example, many materials composed by few-layered graphene oxide flakes in combination with polymers, nanoparticles, and bio-objects have been reported.\textsuperscript{[71–74]} Expansion of GO lattice and local swelling pressure in the range of tens to hundreds of bars range might be sufficient for degradation and break up of these composite materials in case of exposure to conditions of varying humidity or to liquid water.

It is also interesting to discuss the relationship between swelling pressure in GO multilayered materials and driving force in permeation of water across the GO membranes. Water permeation properties of GO membranes are studied most commonly using two methods. Pervaporation setup suggests using liquid water on one side of the membrane while the other side is exposed to moisture-free conditions.\textsuperscript{[75,76]} Water permeation rate of GO membranes in pervaporation has been reported to be the same as in vapor permeation setup when saturated water vapor is used instead of liquid water.\textsuperscript{[9]} In many studies, the driving force of vapor permeation is assumed to be a gradient of water pressure on opposite sides of membranes.\textsuperscript{[77,78]} This pressure gradient (mbar) is significantly smaller compared to the pressure gradient (1–20 bar) used in pressure-driven filtration experiments. Since the permeance of membranes is usually expressed in units which include pressure, the small gradient of pressure due to difference in humidity between feed and permeate streams in pervaporation experiments results in calculations of huge values, e.g., \(\approx80\) 000 L/\((\text{m}^2\text{ bar h})\) even for quite common water flux.
However, it is reported that not the pressure gradient but the rate of water evaporation in pervaporation is the limiting step, which controls the permeation rate.\textsuperscript{[5,54]} The membrane permeation rate depends not on the pressure gradient due to different humidity on the sides of GO membrane, but mostly on the rate of the water evaporation from the surface of the membrane.\textsuperscript{[5]} That is, the same pressure gradient results in higher flow across the membrane if water evaporates faster on the permeate side.\textsuperscript{[5]}

Despite a very small pressure gradient, the water flux is one to two orders of magnitude higher in pervaporation (or vapor permeation) setup as compared to pressure-driven permeation.\textsuperscript{[54]} Several studies postulated existence of “capillary-like” pressure to explain a high flow rate of water inside of GO interlayers.\textsuperscript{[5,53]}

Here we argue that the high flow rate of water in pervaporation setup is related to the closely interconnected effects of hydration force, suction pressure, and swelling pressure in GO membranes. Rapid evaporation of water from the surface of GO membrane exposed to humidity-free conditions (assisted by the high surface area of GO channels\textsuperscript{[54]}) results in the formation of a water-deficient zone on the permeate side. The flow rate across the membrane depends mostly on the gradient in the water content inside of the GO interlayers. The flow of water from water-saturated to water-deficient part of a membrane is driven by suction pressure. The suction pressure developed by hydrophilic materials under confinement conditions also results in the development of swelling pressure.\textsuperscript{[28]} It is known that the suction pressure developed by clay materials can be as high as hundreds of bar in highly compacted (void-free) samples.\textsuperscript{[80]} Qualitative estimation of suction pressure can be done using swelling pressure values provided by our experiments. Suction pressure is developed in the direction of the GO membrane plane, while the swelling pressure is perpendicular to the plane. However, both pressures are originating from the same hydration force. The swelling pressure is measured under the conditions of sample confinement, while maximal suction is achieved when the material is allowed to expand because of hydration. Therefore, it is reasonable to estimate the possible maximal suction pressure developed inside of GO interlayers in the absence of confinement using swelling pressures measured in our experiments (up to 226 bar). The suction pressure of ≈200 bar in combination with rapid removal of water by evaporation to create water-deficient zone on the permeate size can then be proposed as feasible explanation for high vapor permeation and pervaporation rates across GO membranes. The swelling pressure observed for bulk graphite oxide in pure water (≈220 bar) can be considered as a high side estimate for suction pressure.

**4. Conclusion**

The swelling pressure of compacted bulk Hummers graphite oxide was measured in water (226 bar) and ethanol (194 bar). The rate of swelling pressure increase was found to be significantly faster in water as compared to ethanol for both graphite oxide and GO membranes. Swelling pressure was also estimated for GO membranes with thickness in the range of tens μm.

Significant swelling pressure measured (>20 bar) is an important factor in applications, which require confinement or encapsulation of GO membranes. It is also a key factor affecting the change of interlayer distance in GO membranes under external pressure. It can be expected that maximal swelling pressures exceeding 200 bar will be observed in GO membrane samples with thickness comparable to powder samples but with significantly faster kinetics. The expansion of GO lattice under conditions of confinement will be controlled by the balance between external pressure and swelling pressure in liquid water (and other polar solvents). Finally, the swelling pressure can be used as an estimation for the suction pressure developed in GO membranes in pervaporation or vapor permeation applications. It is proposed that hydration force is responsible for a rapid water flow inside of GO inert-layers. The flow of water from water-saturated to water-deficient parts of GO membranes is driven by the suction pressure of tens to hundreds of bars.

**5. Experimental Section**

**Materials**: Commercial graphite oxide by Abalonyx (Norway) was used for swelling pressure tests in a powder form. It was also used as a precursor to prepare GO membranes tested for swelling pressure. Characterization of GO powder was performed by XRD (Figure 3), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). XPS and FTIR are shown in Figures S1 and S2 in the Supporting Information.

**Membrane Preparation**: Graphene oxide membranes were prepared using standard vacuum filtration of aqueous dispersions prepared by sonication of graphite oxide powder. Several membrane samples were tested to study swelling pressure and effect of thickness: Membrane 1—thickness 32 ± 2 μm, weight 41.4 mg, and bulk density 0.75 g cm\(^{-3}\); Membrane 2—thickness 33 ± 2 μm, weight 43.4 mg, and density 0.75 g cm\(^{-3}\); Membrane 3—thickness 80 ± 5 μm, weight 153.5 mg, and density 1.10 g cm\(^{-3}\); Membrane 4—thickness 70 ± 5 μm, weight 111.2 mg, and density 1.0 g cm\(^{-3}\); Membrane 5—thickness 115 ± 15 μm, weight 150.0 mg, and density 0.95 g cm\(^{-3}\); and Membrane 6—thickness 47 ± 3 μm, weight 64.0 mg, and density 0.95 g cm\(^{-3}\).

Swelling Pressure Experiment: Swelling pressure for graphite oxide powder was studied using the standard setup shown in Figure 6. This device (Figure 6) is standard for routine measurements of soils and clays, which are usually available in bulk amounts. The standard soil test is carried out with a large amount of material, typically 10 g compressed into cylinder with diameter 30 mm.

The cell was slightly modified for GO membrane tests. Polymer membrane Omnipore 1 μm thick polytetrafluoroethylene was used instead of the glass filter. Polymer membranes were used to avoid mechanical damage of GO membranes by not entirely smooth surface of standard glass filters. Liquids were supplied through the path on the top of the sample under 0.3 bar pressure. For this purpose, the vessel with the source liquid was placed 3 m above the cell and connected to the assemblage by plastic pipe. To prevent the GO membrane perforation due to the pressure applied by liquid, metallic filter was placed inside of the connecting pipe to cover the membrane. Blank test performed without sample and with only the polymer membranes showed a flow rate across the cell 56 mL h\(^{-1}\). The water and ethanol permeation across the sample was too slow to observe the flow rate. No liquid dropping was observed on the bottom of the cell. This observation is in agreement with similarly slow water permeation across the GO membranes reported in earlier studies.\textsuperscript{[31,36]} The water is removed from the backside of the GO membranes only by evaporation from the surface in the process of vacuum filtration (pressure gradient about 1 bar).\textsuperscript{[3,36]} Experimental error of swelling pressure tests was estimated to be 0.15 bar. More details about swelling pressure cell, error estimation, and reference tests are available in Figures S3 and S4 in the Supporting Information.
The graphite oxide powder samples were vacuum dried prior to the test and loaded into the cell in an amount 5 or 10 g at ambient air humidity conditions. A sample was compacted under 150 bar, the pressure was then released, volume of the sample measured and density of the compacted sample calculated. Membranes are already compacted material with densely packed GO layers. Therefore swelling tests were performed without pressure compaction. The bulk density of GO membranes was calculated using the weight and thickness of the samples. The thickness of the membrane was measured by digital micrometer with flat 5 mm diameter tips. The standard procedure for experiments is to apply 1.5–5 bar pressure to the precompacted sample and add water or ethanol through the connecting pipe. The pressure inside of the cell increases due to swelling-induced expansion. Each swelling test was performed to observe pressure stabilization.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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Data available in article supplementary material.

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**Figure 6.** Scheme and image of swelling pressure test apparatus. The assemblage includes two rigid glass filters, a stainless steel ring, a stamp with the liquid path, a load cell with a maximum force of 30 kN, and a fixing frame. A sample is placed between two filters. External pressure is applied and released to measure the volume of the sample. The stamp is placed on a glass filter with a load cell on top. The frame is fixed with bolts by creating initial pressure in the system. Water or other liquid is provided to the sample through the hole in the filter.
