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## ARTICLE

## Swelling of graphene oxide membranes in alcohols: effects of molecule size and air ageing.

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**Abstract:** Swelling of Hummers graphene oxide (HGO) membranes in a set of progressively longer liquid alcohols (methanol to 1-nonanol) was studied using synchrotron radiation XRD after on air ageing over prolonged periods of time. Both precursor graphite oxides and freshly prepared HGO membranes were found to swell in the whole set of nine liquid alcohols with increase of interlayer spacing from  $\sim 7\text{Å}$  (solvent free) up to  $\sim 26\text{Å}$  (in 1-nonanol). Pronounced effect of ageing on swelling in alcohols was found for HGO membranes stored on air. The swelling of HGO membranes aged for 0.5–1.5 years shows progressively slower kinetics, non-monotonous decrease of saturated swelling in some alcohols and completely disappeared for alcohol molecules larger than hexanol. Moreover, the HGO membranes stored at ambient conditions for 5 years showed nearly complete absence of swelling in all alcohols but preserved swelling in water. In contrast, precursor graphite oxide powders showed unmodified swelling in alcohols even after 4 years of ageing. Since the swelling defines size of permeation channels, the ageing effect is one of important parameters which could explain strong scatter in reported filtration/separation properties of GO membranes. The time and conditions of air storage require standardization for better reproducibility of results related to performance of GO membrane in various applications. The ageing of GO membranes can be considered not only as a hinder/degradation for certain applications, but also as a method to tune swelling properties of HGO membranes for better selectivity in sorption of solvents and for achieving better selective permeability.

### Introduction

Multilayered graphene oxide (GO) laminates in a form of papers<sup>1</sup>, thin films<sup>2</sup> or membranes<sup>3–5</sup> attracted a lot of attention over past 6 years. The membranes were proposed for applications e.g. for gas separation<sup>6</sup>, nanofiltration,<sup>7–9</sup> separation of solvent mixtures<sup>10, 11</sup>, as a toxicant barrier<sup>12</sup> and for water desalination.<sup>13</sup>

Graphite oxides are hydrophilic layered materials which can easily be dispersed in polar solvents.<sup>7, 14</sup> Drop casting<sup>5</sup> and spin coating<sup>15</sup> are the methods commonly used for preparation of GO thin films while vacuum filtration provides free standing membranes.<sup>16, 17</sup> Most of the applications cited above are enabled by ability of GO multilayers to swell in polar solvents similarly to their precursor graphite oxides.<sup>18–20</sup>

Swelling of GO membranes is directly related to the size of “permeation channels” which enable diffusion of solvents and solutions. The interlayer distance of GO structure is typically studied

using X-ray Diffraction (XRD),<sup>14, 21, 22</sup> direct measurements of film/membrane thickness<sup>23</sup> or quantitative evaluation of solvent vapor sorption.<sup>24–26</sup> Simultaneous evaluation of multilayered GO film thickness and amount of sorbed solvent can be done using Neutron Reflectivity (NR) methods.<sup>15, 27</sup>

Swelling of precursor graphite oxides in polar solvents was studied in detail over past 150 years, most typically in water,<sup>21, 28</sup> alcohols<sup>29–32</sup> or amines.<sup>33–35</sup> The swelling of graphite oxides depends on synthesis method, most notably for materials prepared by Brodie’s and Hummers’s oxidation routes.<sup>36</sup> It is known that interlayer distance of Brodie graphite oxides immersed in liquid alcohols increases proportionally to the length of molecules providing multilayered intercalation<sup>30</sup> with interlayer distances up to  $\sim 50\text{Å}$  for 18-carbon molecules.<sup>29</sup>

However, recent studies revealed that the swelling of GO membranes can be significantly different compared to precursor graphite oxides.<sup>16, 17</sup> The swelling of GO membranes in e.g. liquid ethanol was reported with significant scatter providing  $d(001)$  values in the range  $\sim 11\text{–}17.7\text{Å}$ .<sup>10, 16, 37, 38</sup> Swelling of HGO membranes was also reported once for several other alcohols: 1-propanol, 1-butanol and 1-pentanol.<sup>10</sup> No systematic studies are so far available for swelling of either Hummers graphite oxides or GO membranes in larger alcohols.

Large scatter can be found in literature also for many other properties of GO membranes, including two orders of magnitude difference in permeation rates<sup>39</sup>. Recent studies emphasized strong

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need for standardization of parameters affecting performance of GO membranes, e.g. difference in oxidation degree, size and shape of GO flakes, defects etc.<sup>39,40</sup>

Little attention was so far paid to effects of GO membrane ageing.<sup>41, 42</sup> Metastability of GO structure was reported for thin films but only over short periods of time (100 days) and mostly using the X-ray Photoelectron Spectroscopy (XPS) which provides information about 1-2 surface layers of material.<sup>43</sup> To our knowledge, the ageing of GO membranes during the on air storage was never studied using characterization of bulk material properties.

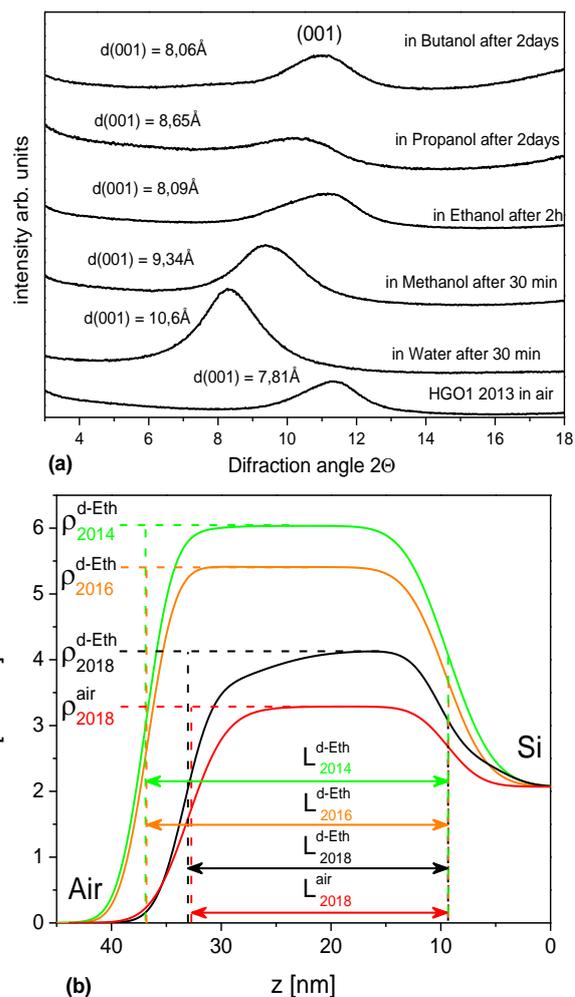
Here we studied GO membranes prepared in 2012-2017<sup>16</sup> and freshly prepared samples for swelling in a set of nine alcohols (from methanol to 1-nonanol). Prolonged storage of GO membranes on air is found to result in progressively slower kinetics of swelling, non-monotonous decrease of saturated swelling in some alcohols, and complete absence of swelling in alcohols after certain period of ageing. At the same time no ageing effect was found for swelling of precursor graphite oxide powders even after 4 years of on air storage. Therefore, the time and conditions of air storage need be considered for better reproducibility of GO membrane research.

## Results and discussion

The GO membranes were studied in our group starting from 2012,<sup>16, 17, 24, 44</sup> including characterization of swelling in liquid water, ethanol and water-ethanol mixtures.<sup>16</sup> The remaining pieces of the same membrane samples were stored on air up to five years and tested again to verify for possible ageing effects.

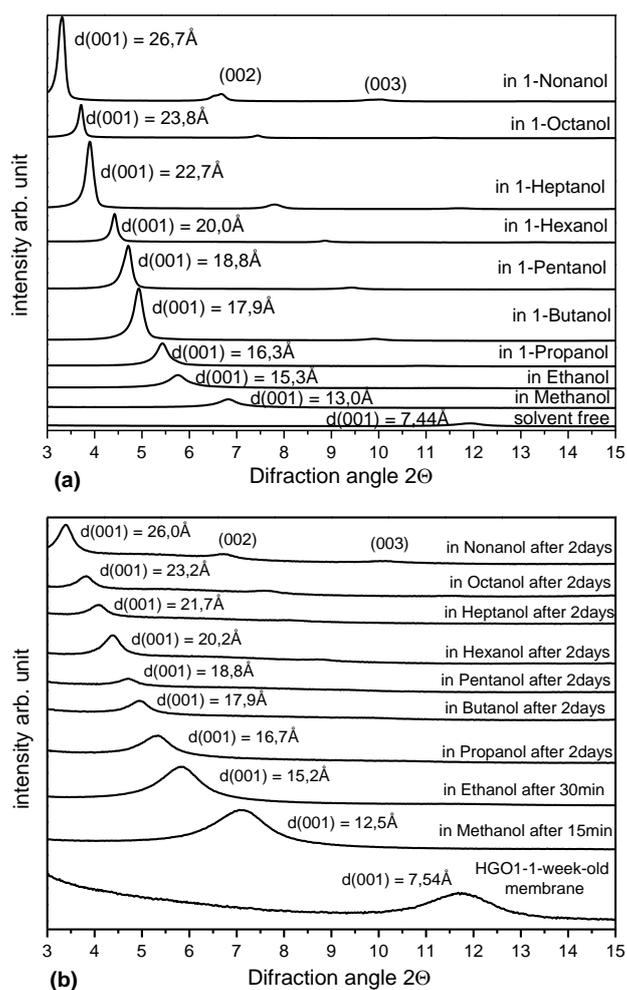
Remarkably, the 5-years old sample showed nearly complete absence of swelling in ethanol and larger alcohols (**Figure 1**). The  $d(001)$  of HGO1 membrane back in 2012 was found at  $7.7\text{\AA}$  in solvent free state and in liquid water respectively. The  $d(001)$  of 5 years old HGO1 membrane was found to be nearly unchanged ( $7.8\text{\AA}$ ) but immersion in ethanol resulted in lattice expansion only up to  $8.1\text{\AA}$ . However, immersing old sample into water provided  $d(001)$  value of  $10.6\text{\AA}$  ( $12.3\text{\AA}$  back in 2012) thus demonstrating smaller but still significant swelling. Very similar results were observed also for HGO1 thin film studied for swelling in saturated deuterated d6-ethanol vapours using NR method three times with intervals of two years (see SI file). The sorption of d6-ethanol decreased from  $0.30\text{ mol/formula unit (f.u.)}$  to  $0.07\text{ mol/f.u.}$  after four years of on air storage and  $d$ -spacing calculated from change of films thickness dropped from  $10.0\text{\AA}$  to  $8.6\text{\AA}$ . Note that the  $d(001)$  found from this film at ambient air conditions remained almost unchanged ( $8.1\text{\AA}$  and  $8.3\text{\AA}$  for pristine and 4 years aged film). Moreover, we observed that films prepared using freshly prepared aqueous GO dispersion and using the same dispersion after two years of storage showed no difference in swelling properties.

Almost complete absence of swelling in ethanol, 1-propanol and 1-butanol revealed in our experiments with aged HGO membrane in combination with good swelling in water is rather surprising and not trivial result. Therefore, we studied swelling of freshly prepared GO membranes in a set of nine alcohols (methanol to 1-nonanol) and swelling of precursor HGO powder samples as a reference.

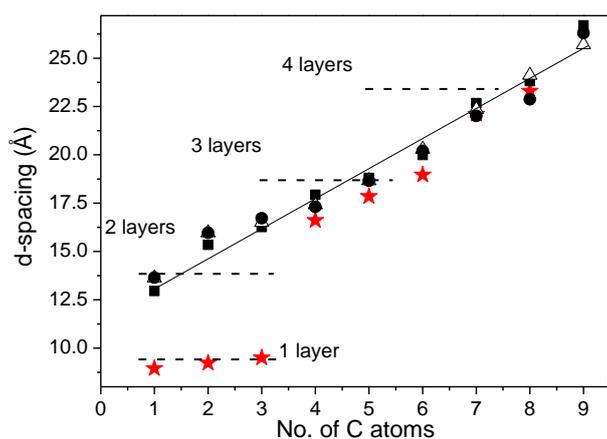


**Figure 1.** a) Saturated swelling of HGO1 membrane sample air aged for 5 years. b) HGO1 film swelling in saturated d6-ethanol vapor after 2 and 4 years of air storage. Modeled Scattering Length Density (SLD) profiles calculated using NR scans for the HGO1 film (see SI file). L corresponds to film thickness and change in  $\rho$  is proportional to amount of sorbed d6-ethanol.

The swelling of three tested graphite oxide precursors (HGO1, HGO2, HGO3, see SI file) were found to be nearly identical (**Figure 2a**). **Figure 2b** shows that *saturated* swelling of 1 week old HGO1 membrane is very similar to swelling of precursor HGO powder in all alcohols. Remarkably the general trend found for swelling of Hummers graphite oxide at ambient temperature shows significant difference compared to Brodie graphite oxide, most remarkable for small alcohols (**Figure 3**). Swelling of HGO in methanol, ethanol and 1-propanol is significantly stronger compared and *corresponds* to intercalation of at least 2-3 layers of solvent molecules. Note that the swelling of Hummers graphite oxide determined using  $d(001)$  should not be directly interpreted using number of intercalated layers. The position of (001) reflection of Hummers graphite oxide is known to increase upon the cooling due to effects of interstratification and intrastratification.<sup>32</sup> That is in strong contrast to Brodie graphite oxide which shows sharp transitions between e.g. 1-layer and 2-layer methanol solvate structures upon changes of temperature and pressure.<sup>31, 36</sup>

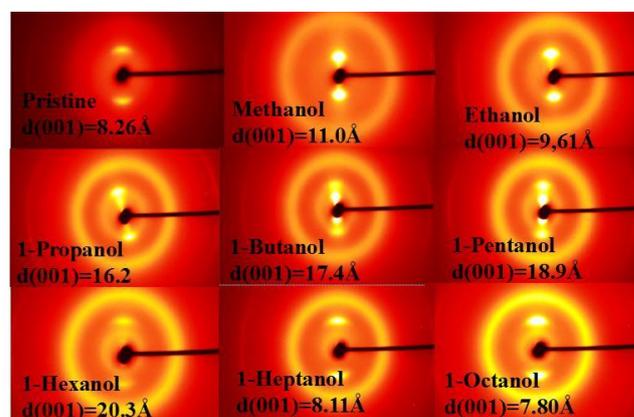
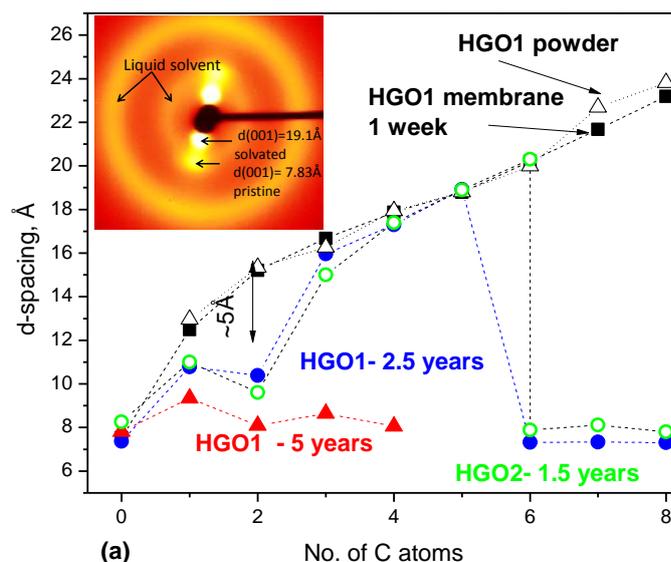


**Figure 2.** XRD patterns recorded from of HGO1 samples immersed in excess of liquid alcohols: a) powder b) freshly prepared membrane (1 week) (CuK $\alpha$  radiation)



**Figure 3** Interlayer distance provided by d(001) of HGO1 (■), HGO2 (●), HGO3(Δ) powder samples and BGO powder (★) (ref.<sup>30</sup>) in liquid alcohols with number of carbon atoms C=1-9 (methanol to 1-nonanol). Dashed lines show approximate swelling levels corresponding to layer by layer intercalation of alcohols

Our experiments demonstrate that small alcohol molecules like methanol and ethanol diffuse into HGO membranes structure rapidly. However, in contrast to rather rapid swelling of powders (saturation achieved within few minutes after immersion) rather slow kinetics of swelling was observed for HGO membranes in large alcohols (6 carbon atoms and higher). Moreover, the HGO2 and HGO3 membranes showed no swelling in largest of alcohols (1-nonanol and 1-octanol) (see SI file). The formation of solvate phase in larger alcohols is found first at near surface layers of GO structure while the inner part remains unaffected for certain period of time.



**Figure 4** a) Interlayer distance (d(001)) for HGO1 powder (Δ), membrane immersed in liquid alcohols: freshly prepared (1 week) sample (■), sample stored on air for 2.5 years (●), sample stored on air for 5 years (▲). Inset shows 2D XRD image ( $\lambda = 0.30996\text{Å}$ ) recorded from HGO2 membrane in 1-pentanol after 7.5 hours of immersion. b) XRD images ( $\lambda = 0.30996\text{Å}$ ) recorded from HGO2 membrane after 23-24 hours of immersion in liquid alcohols (see integrated scans and data for other samples in SI file)

For example, experiment with freshly prepared HGO1 membrane immersed in 1-heptanol showed (001) reflections of both swollen and pristine phases. The position of the (001) reflection from solvated phase did not shift significantly with time (21.5Å to 22.1Å in 12 hours) but the relative intensity was increasing over the period of hours reflecting penetration of solvent into the subsurface parts of multilayered structure (details in SI file)

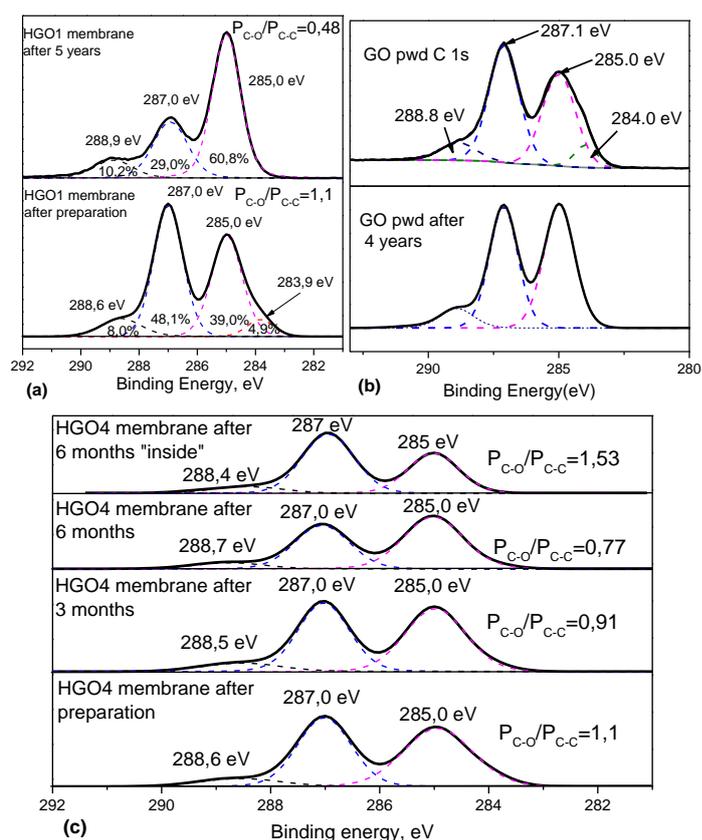
The difference between swelling of HGO membranes and powders becomes stronger for membranes stored over longer periods of time (0.6-2.5 years). The ageing of HGO1 membranes for 1-2,5 years results in two non-trivial effects. First is absence of swelling in 1-hexanol, 1-heptanol, 1-octanol and 1-nonanol (Figure 4a). Second effect is smaller swelling in ethanol providing  $d(001)=10.4\text{\AA}$  which is  $\sim 5\text{\AA}$  smaller compared to freshly prepared HGO1 membranes. Remarkably, the swelling in 1-propanol, 1-butanol and 1-pentanol was almost unaffected by the ageing for 2.5 years. Similar data were also recorded using HGO2 membrane sample studied for swelling in alcohols after storing it for 1.5 years (see SI file). Nonhomogeneous swelling of HGO membrane interlayers was detected using 2D XRD images which reveal significant diffuse scattering. The 2D image shown in Figure 4a shows two pairs of spots from (001) reflections of pristine and solvated phase, diffuse scattering and rings from liquid solvent. The straight line of diffuse intensity provides evidence for presence of continuous distribution of interlayer distances.

The mechanism behind the non-trivial change in swelling properties of HGO membranes was investigated using characterization of freshly prepared and aged samples. XPS spectra recorded from the same piece of membrane as in ref<sup>16</sup> after five years of storage showed significant ageing effects (Figure 5a).

The relative intensity of three main peaks in the C1s XPS spectra has changed dramatically while the C/O ratio increased from 2.49 to 3.03. Chemical transformation of HGO material over long period of time e.g. due to metastability effect reported in ref. could be suggested to explain evolution of the spectra.<sup>43</sup> However, the XPS data provide information only about 1-2 surface layers of multilayered membrane and could be strongly affected by surface related sorption of various molecules from air. Surface contamination, e.g. sorption of hydrocarbons, would contribute to increased intensity of C-C peak (285.0 eV). However, surface sorption would affect both graphite oxide powder and GO membranes very similarly.

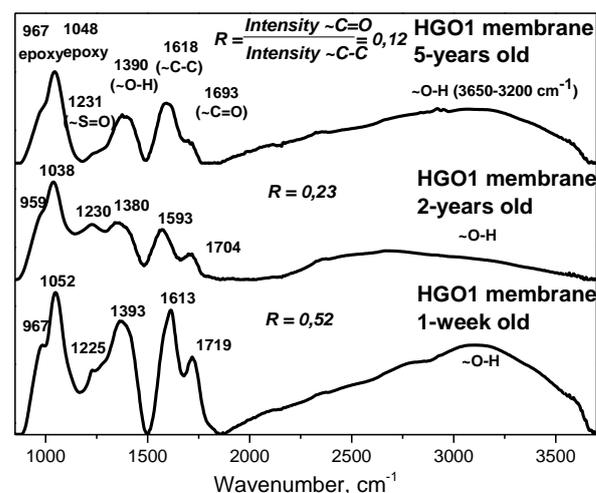
Surprisingly, the changes in XPS spectra of precursor graphite oxide after 4 years of air storage appeared to be rather minor compared to the changes observed in spectra recorded from the aged membranes (Figure 5b).

The effect of surface modification is also obvious in the XPS spectra recorded from membranes aged for several months (Figure 5c). The relative intensity of peaks typically assigned to C-C and C-O (284.5 eV and 286.5 eV respectively) gradually changed following air storage. However, the change in XPS spectra observed after 6 month of air storage was found to affect only surface layers of the membrane. XPS spectra recorded from the inner part of the same membrane sample showed relative intensity of main peaks typical for freshly prepared sample (Figure 5c). Therefore, the change of surface properties due sorption of some molecules from air also cannot be ruled out.



**Figure 5.** a) C1s part of XPS spectra of HGO1 membrane measured in 2013<sup>16</sup> and after 5 years of ageing at ambient conditions. b) XPS spectra recorded from HGO1 powder sample shortly after synthesis (C/O=2.47) and 4 years later after on air storage (C/O=2.38) c) C1s XPS spectra of HGO membrane measured 1 week, 3 month, 6 month after preparation on the surface and after mechanical removal of surface layers ("inside").

The FTIR spectra of aged samples showed different relative intensity of some main peaks, most notably decrease in intensity ratio for peaks due to C-C and C=O vibrations (Figure 6).



**Figure 6** FTIR spectra recorded from HGO1 membranes freshly prepared and aged for 2 years and 5 years.

Double bonded oxygen functional groups (carbonyls and carboxyls) can be found on the edges of GO flakes or on the edges of holes or vacancies on their planar part. Strong decrease in intensity of C=O peak in FTIR spectra indicates that some chemical modification of the GO flake edges occurs as a result of ageing and it is not related only to surface part of the membrane sample.

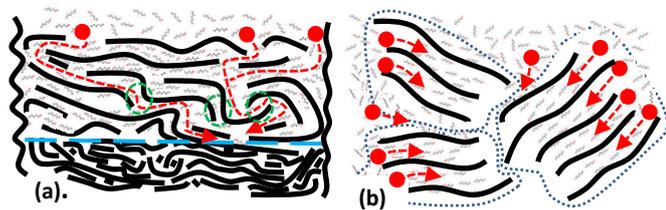
Since the swelling of precursor graphite oxides remains nearly unchanged even after many years of air storage, we suggest that the ageing of membranes is likely to occur due to interactions between GO flakes in the multilayered structure rather than due to intrinsic metastability of GO. The difference between swelling of powders and membranes is evident already for freshly prepared samples. Graphite oxides are synthesized starting from graphite powder and preserve original shape and size of graphite grains.<sup>28</sup> The entrance points of all interlayers are open for interaction with bulk liquid surrounding the grains of graphite oxide. In contrast, GO membranes are formed by random re-stacking of individual sheets with nearly complete overlap of all edges. The solvent must diffuse along zigzag pathway starting from the surface of membrane and around the overlapped edges of flakes to penetrate into sub-surface layers (Figure 7).

The results presented above suggest following **two-step mechanism** of membrane swelling:

- swelling of interlayers directly exposed to bulk solvent occurs rapidly achieving saturation value of interlayer distance at least within minutes. Graphite oxide powders swell in one step.
- penetration of solvent into subsurface layers occurs across/around overlapped flake edges. The overlaps (“junctions”) provide major limitation for diffusion of solvent into the bulk body of membranes. The overlaps also provide size limitation for penetration of larger molecules.

The GO flake edge overlap regions (interlayer “junctions”) are likely to become less flexible in the membranes stored for prolonged period of time. The swelling of HGO membranes in the largest alcohols ceases over the time as a result of decreased ability of these interlayer junctions to expand.

The XPS and FTIR data (Figures 5,6) demonstrate that the ageing of GO membranes starts from surface and extends into the deeper sub-surface part of the membrane with time. Therefore, the ageing can be connected to interaction of GO with air mediated by sorption of water (10-50 wt%, proportionally to humidity<sup>24,28</sup>).



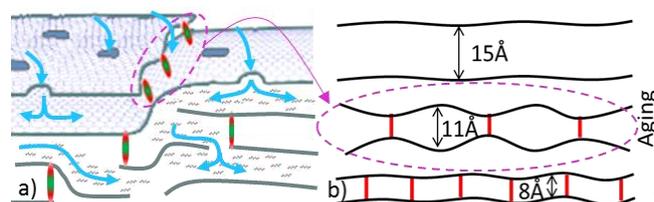
**Figure 7.** Schematic representation of difference in packing of GO flakes in HGO membranes and precursor powders. a) Zigzag pathway of solvent molecules is typical for the membranes whereas the rate of diffusion is limited by the “junction” fronts along the overlapped flake edge (green ovals). b). Graphite oxide structure provides entrance points, “gates” (●), to most of inter-layers directly accessible from the bulk liquid solvent.

A number of possible air contaminants might dissolve in water. These molecules will diffuse into the membrane interlayers and stack/react at the junction points between overlapped edges of GO flakes.

The chemical interaction of GO edge functional groups (e.g. carboxyl's) with neighboring GO flakes is more likely to occur at the regions of edge overlaps. If the number of connection points at the junction regions is small the GO lattice is still capable to swell in almost full scale. When more connection points are added along the edges the openings available for diffusion of molecules become smaller. In the end only the smallest molecules (water) penetrate around the edge regions (Figure 7).

It is unclear at the moment why the membranes aged for 0.6-2.5 years show significant decrease of swelling in ethanol (from ~15Å in fresh to ~9.5-10.5Å in aged samples) while the swelling in larger 1-propanol, 1-butanol and 1-pentanol remains unchanged. In fact, the decrease of d(001) of HGO in ethanol below ~15Å is rather straightforward indication of the bulk membrane ageing. For example, the samples used in our earlier study of HGO membrane swelling in water/ethanol mixtures were clearly affected by ageing since the d(001) found in pure ethanol was found at ~10.7Å for two different membranes.<sup>16</sup> Testing various membrane samples for swelling in ethanol revealed that in some case the ageing can be detected already after 6 month of air storage, in other samples swelling remained unchanged for longer period of time up to 1 year.

The rate of GO membranes ageing is likely to depend on many parameters of sample storage, e.g. humidity levels, variations of humidity, temperature etc. It cannot be ruled out that similar ageing occurs much faster (weeks) at different sample storage conditions, e.g. at very low or very high humidity or in colder/warmer climate. The difference between swelling of graphite oxide powder and HGO membranes was also found to be stronger for samples with larger average flake size (0.12µm for HGO1 vs 0.28µm and 0.33µm for HGO2 and HGO3 sample respectively, see SI file). Note that flake size of 0.1-0.3 µm is most common in GO membrane research due to break up of larger flakes in process of dispersion preparation by sonication. This type of membranes was recently named as “conventional” to distinguish from membranes composed by larger flakes.<sup>45</sup>



**Figure 7.** a) Schematic representation of solvent permeation path across GO membrane multilayers with obstacles formed as a result of ageing along the edges of GO flakes. b) Schematic illustration how interconnections of GO flake edges could decrease maximal interlayer distance under swelling conditions.

Results presented in this study demonstrate that ageing must be considered as one of key parameters which affect swelling and,

as a result, permeation properties of HGO membranes. It is known that permeation rates reported for GO membranes in various studies are different by two orders of magnitude.<sup>39</sup> Therefore, ageing needs to be added to the list of parameters which affect GO membranes performance and require standardization.<sup>40</sup>

Most of the studies related to properties of GO membranes do not report exact time and conditions for their storage after preparation.

## Conclusions

In summary, both precursor graphite oxides and freshly prepared HGO1 membranes are found to swell in the set of liquid alcohols (from methanol to 1-nonanol). The increase of interlayer spacing is found to be proportional to the size of alcohol molecules suggesting multilayered intercalation (up to  $\sim 26$  Å in 1-nonanol).

Pronounced ageing effects were found for membranes stored on air. The aging starts on the surface of the multilayered structure and slowly penetrates into the deeper regions. The lattice expansion due to swelling of HGO in ethanol and methanol become significantly smaller with time and disappeared for 1-hexanol and larger alcohol molecules already after 0.6-2 years of ageing. The samples stored at ambient conditions for 5 years showed nearly complete absence of swelling in alcohols but preserved significant swelling in water. The ageing of HGO membranes can be considered as a method to tune swelling properties of HGO membranes for better selectivity in sorption of solvents and selective permeability.

The ageing of HGO membranes must be considered as one of the major parameters which effect their permeation properties. The rate of ageing is likely to be affected by the properties of membranes vs conditions of sample storage and standardization is required in order to achieve better reproducibility of experimental results related to GO membrane applications.

## Experimental Section

The powder samples of commercial ACS Material graphite oxide (HGO1) and several batches of graphite oxides synthesized in our laboratory (HGO2, HGO3, HGO4) were used to prepare membranes by vacuum filtration of aqueous dispersions. Characterization of precursor graphite oxides is available in SI file (XPS, XRD, FTIR). The degree of oxidation was found to be very similar with C/O in the range 2.30-2.47. Some HGO1 powder purchased in 2013 was re-evaluated in 2018 for ageing effects. Details of membrane preparation procedure were the same as in our previously published studies.<sup>17</sup> (see in SI file for details). Several membrane samples prepared using HGO were re-characterized again after 1-5 years of air storage. The thickness of membranes varied in the range 5-50  $\mu\text{m}$ . More specifically, the data shown in Figure 3 were collected using 5  $\mu\text{m}$  thick membrane. Thickness of membrane shown in Figure 4: 5  $\mu\text{m}$  1 week old HGO1, 6  $\mu\text{m}$  for 2.5 years old HGO1, 18  $\mu\text{m}$  for HGO2 and 34  $\mu\text{m}$  for 5 years old sample. The membrane samples were stored at ambient humidity in the lab or office environment with typical humidity of 15-40% and temperatures 20-25°C.

HGO1 dispersion was used to prepare dispersions spin coated on Si blocks and studied using NR for ethanol and water sorption.<sup>15</sup> The sample of HGO1 thin film on Si was characterized 3 times over 4 years for sorption of d6-ethanol from saturated vapour. Neutron reflectivity experiments were performed in a specially designed humidity cell at the reflectometer SuperADAM at the Institute Laue-Langevin (ILL), Grenoble, France using a monochromatic beam with wavelength  $\lambda=5.19$ Å, details are available in SI and elsewhere.<sup>27</sup> XRD characterization of graphite oxides and HGO membranes immersed in excess of liquid solvents was performed using in-house diffractometer PANalytical X'pert diffractometer with CuK $\alpha$  radiation in reflection mode and synchrotron radiation in beamline ID 11 ESRF, Grenoble, France with  $\lambda = 0.30996$ Å. Several scans were typically recorded for solvent immersed samples until saturated swelling is achieved (5 min-2 days). Chemical composition of membrane was tested by XPS and FTIR spectroscopy, AFM was used to evaluate flake size distribution see details in SI.

## Conflicts of interest

There are no conflicts to declare.

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