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Original article

Ageing of graphene oxide thin films: the dynamics of gas and water vapors permeability in time

Ekaterina A. Chernova[1,a], Konstantin E. Gurianov[1,b], Mikhail V. Berekchiian[1,c], Victor A. Brotsman[2,d], Rishat G. Valeev[3,e], Olesya O. Kapitanova[2,f], Alina V. Kirianova[1,g], Alexey V. Lukashin[1,h]

[1]Lomonosov Moscow State University, Faculty of Materials Science, Moscow, Russia

[2]Lomonosov Moscow State University, Faculty of Chemistry, Moscow, Russia

[3]Udmurt Federal Research Center of the Ural Brunch of Russian Academy of Sciences, Izhevsk, Russia

[a]chernova.msu@gmail.com; [b]gurianovke@yandex.ru; [c]mikhail.berekchiyan@yandex.ru;
[d]brotsman_va@mail.ru; [e]rishatvaleev@mail.ru; [f]olesya.kapitanova@gmail.com,
[g]vov-lena2010@yandex.ru; [h]alexey.lukashin@gmail.com

Corresponding author: Ekaterina A. Chernova, chernova.msu@gmail.com

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ABSTRACT Composite membranes are formed based on ultrathin 20 nm-thick selective layers of graphene oxide nanoflakes deposited on porous anodic alumina substrates. The long-term dynamics of permanent gases transport and water vapor permeability across the composite membranes is measured during 240 days (8 months). It is revealed that the permeability towards permanent gases remains nearly constant during a prolonged period of time. Contrary, water vapor flux decreases rapidly within the first 30 days from the membrane preparation moment and reaches about 80% of permeability loss during 8 months. The rapid decrease of membrane permeability during the first month could be attributed to a gradual packing of graphene oxide nanoflakes, particularly, locating in the surface sublayers, into more tight microstructure due to the evaporation of remaining solvent (membrane drying) under ambient conditions. Further decrease in permeability during more prolonged time could be caused additionally by deoxygenation of surface GO nanoflakes preventing water vapors diffusion into the GO film. This phenomenon, the so called "ageing" accompanies graphene oxide thin films similarly to some types of highly-permeable polymers. Holding the aged membrane under saturated water vapors, and even liquid water, didn't allow one to revitalize completely its permeability. The obtained results should be taken into account when designing membranes and other devices based on graphene oxide and its derivatives.

KEYWORDS graphene oxide nanoflakes, anodic alumina, membrane ageing, dehumidification, water vapor transport.

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1. Introduction

At present time, graphene oxide (GO) is considered as an advanced material both for the preparation of graphene, and as a building block for a variety of applications including the design of membrane materials [1], sensors [2], and catalytic platforms [3]. The lamellar microstructure of graphene oxide is represented by an assembly of stacked nanoflakes richly decorated with functional oxygen-containing groups endowing GO with an ability to separate water vapors from gas mixtures for a variety of industrial applications. For instance, GO-based composite membranes can achieve water vapor permeance of 10–60 $m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$ in the relative humidity range of a feed stream from 40 to 90% and can be used for the dehumidification of gases with moderate-to-high concentrations of water vapor [4, 5]. Moreover, by adjusting oxygen-to-carbon ratio (C/O ratio), it is possible to tune the permeance-selectivity characteristics of GO-based membranes [6]. On the other hand, functional properties of GO composite membranes strongly depend on the packing architecture and ordering of GO nanoflakes, which are pre-determined by methods of GO thin films preparation including filtration, spin/spray-coating, solvent evaporation, etc [7].

All the parameters discussed above are usually reported for the freshly prepared graphene oxide membranes. However, as every material, GO can be prone to dynamical changing of its characteristics with time which can influence on its functional characteristics. This phenomenon, the so called "ageing", for instance, accompanies microporous polymers and manifests itself in tight packing of macromolecules in a polymeric membrane and appears as a dramatic decrease in permeability [8]. Recently, ageing has been also reported for graphene oxide. To date, ageing of GO was reported for GO films [9], powders [10] and suspensions [11]. For instance, dynamics in swelling behavior was reported for 5–50 μm thick GO films prepared by Hummers' method (HGO) aged during 1–5 years under ambient conditions [9]. It was shown that even after 0.6–2 years of air storage, the swelling degree of HGO in ethanol and methanol became drastically smaller with time, and the swelling completely disappeared for larger alcohol molecules. Moreover, the 5 years-old samples did not show any signs of lattice expansion when immersed in alcohols but preserved a good swelling in liquid water [9]. The observed results were attributed to gradual deoxygenation of GO nanosheets covering the surface of graphene oxide films accompanied by drying caused by solvent evaporation from the GO film. In other work, the dynamics of structural and thermal characteristics with time for HGO powders stored during 2 years at ambient conditions was studied [10]. It was revealed that average d-spacing of the samples decreased from 0.660 to 0.567 nm, while the C/O ratio of graphene oxide increased from 1.96 to 2.76 which was attributed to the desorption of oxygen-containing groups from GO nanoflakes. Recently, a long-term studying of ageing of high-concentrated (10 mg/mL) aqueous GO suspensions has revealed that within the first year of storage both the viscosity and dynamic moduli of suspension increased with time [11]. The authors attributed this result to gradual time-dependent oxidation of GO nanoflakes in suspension, however, it is a matter of dispute and requires more detailed experiments.

The analysis of the literature data has shown that the phenomenon of ageing was considered for GO mainly in terms of its physico-chemical and rheological properties, while the dynamics of GO membranes permeability was not taken into account. In this work we report on the dynamics of water vapor and gas transport characteristics in graphene oxide-based membranes. The results are important not only for the design and storage of GO-based membranes, but also for the development of platforms for sensors, catalysis and other devices based on GO thin films.

2. Experimental part

Suspensions of graphene oxide nanosheets were prepared using the improved Hummers' method [12] by oxidizing medium flake graphite with graphite:KMnO4 ratio of 1:6; the detailed description of the method is presented in our previous paper [6]. The suspensions were purified from residual inorganic ions by dialysis during 30 days under constant stirring. The removal of sulfate-ions from the resulting GO suspensions was controlled by conductometry and XPS. The obtained suspension of graphene oxide was denoted as MFGO (medium-flake graphene oxide). The average size of MFGO nanosheets obtained by the described procedure is 750±100 nm [6].

The composite membranes were prepared in the form of thin MFGO films deposited onto porous anodic aluminum oxide (AAO) membranes with pore diameter of $\sim$80 nm and a thickness of 100 μm. The detailed description of the AAO films preparation and their gas permeance is given in [13, 14]. Briefly, the porous AAO supports were prepared by a standard anodic oxidation procedure of high purity aluminium foils (99,999%) in 0.3M $H_2C_2O_4$ at 120V followed by selective etching of aluminum and removing a barrier layer to obtain aluminum-reinforced AAO supports with the average N2 permeance of 90–100 $m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$ [15]. To prepare composite membranes, the water-methanol (H_2O:CH_3OH vol. ratio of 1:1) suspension of MFGO with the concentration of 1.0 mg/mL was prepared. The thin films of MFGO were formed by successive deposition (3 times, aliquot of 40 ml) and spin-coating of the MFGO suspension onto porous AAO supports under slight vacuum suction ($\sim$30 kPa) at the rotation rate of 1500 rpm.

The X-ray photoelectron (XPS) spectra (overview and region C1*s* and O1*s)* of the composite membranes were registered on SPECS (Germany) instrument by employing MgK-α excitation (E_{ex}=1254 eV). The resulting spectra were calibrated to pure graphite C1*s* energy (284.6 eV) and were treated using CasaXPS software package. For spectra deconvolution, Shirley type background and mixed Gauss (70%)-Lorentz (30%) functions were used (the FWHM was kept fixed for all the spectral components). The C–C band subdivision into sp^2–C, sp^3–C components was neglected because of an insufficient spectral resolution [16]. Also, spectral component corresponding to O–C=O groups was not taken into consideration due to its low intensity.

Scanning electron microscopy (SEM) studies of a bottom part and cross-sections of the composite membranes were performed using Nvision 40 (Carl Zeiss) microscope. The obtained SEM micrographs were statistically treated using ImageJ software to extract the average thickness of the MFGO selective layer. To estimate the thickness of a single MFGO nanosheet, atomic-force microscopy (AFM) was employed. A diluted suspension of GO nanosheets was deposited on mica, dried carefully and subjected to AFM analysis using N-TEGRA NT-MDT instrument.

The transport characteristics of MFGO-based membranes were measured towards a set of permanent gases (H_2, N_2, O_2, CO_2, CH_4, C_4H_{10} and SF_6) and water vapors in dynamic and steady modes depending on the relative humidity (RH) of the feed streams [17]. A measurement cell consisting of a feed chamber and calibrated permeate chamber was employed. The permeate chamber was evacuated to a residual pressure of less than 0.1 mbar. Then, the stream of the measured gas was introduced into the feed chamber and a gradual pressure increase of the gas inflowing into the permeate chamber was registered in the form of a pressure-time curve. To study the transport of water vapors in a dynamic mode, wet nitrogen flow (relative humidity $\sim$100%) was used as a feed stream and a gradual pressure growth inside the permeate chamber was registered until the time when the pressure level exceeding the saturated H2O vapors pressure ($\sim$5 kPa, at

TABLE 1. XPS peak assignment for MFGO-based selective layer of the composite MFGO-based membrane

Sample	Spectral region	Band assignment	Initial GO		
			XPS component	Component content, %	C:O ratio
MFGO/AAO composite membrane	C1s	C–C	284.60	47.31	1.8:1
		C–O	286.96	42.78	
		C=O	288.30	9.91	
	O1s	C=O	532.74	26.59	
		C–O	531.01	73.41	

292K) was achieved. The fluxes of permanent gases as well as water vapors in a dynamic mode were calculated using a slope of the linear part of the pressure-time dependence.

Water vapor permeability under steady mode was measured under varied relative humidity of the feed stream. The detailed protocol was described earlier in our paper [18]. Briefly, a gas flux with a controlled humidity (feed stream pressure = 1 bar) was introduced into the feed side of the composite membrane, while the permeate side of the membrane was blown by He flux (pressure = 1 bar). The humidity and temperature of both gas fluxes were controlled using HIH-4000 sensors (Honeywell, USA). The experiments were performed at the temperatures of 23–25°C.

3. Results and discussion

According to SEM results (Fig. 1a,b), the selective layer of the MFGO-based composite membrane reveals its inherent wavy texture with large wrinkles more than 3 μm in length owing to corrugated shape of individual MFGO nanosheets composing the entire microstructure. According to the statistical analysis of the membrane cross-section, MFGO-based selective layer is uniform and ultrathin with the average thickness of 20 nm and is spreading uniformly on the porous AAO substrate. AFM results reveal that the average thickness of a single MFGO nanoflake is 0.925 nm which stays in the typical thickness range for single-layer GO nanosheets (0.8–1.2 nm depending on oxidation degree) [23] (Fig. 1c,d). Thus, the membranes in this work are prepared from high-quality single-layer graphene oxide. As has been shown by us earlier, the typical d-spacing for MFGO films is 0.83 nm under ambient conditions [18]. To estimate the number of MFGO nanosheets in the membrane, the thickness of MFGO film (20 nm) could be divided into a typical d-spacing [9], giving an average number of MFGO nanosheets equal to 24.

According to X-ray photoelectron analysis (Fig. 1e,f, Table 1), the MFGO-based selective layer of the composite membrane has the oxidation degree (C/O ratio) of 1.8 which is typical for the graphene oxide samples obtained by improved Hummers' method with graphite/$KMnO_4$ ratio of 1:6 and suggests the high quality of the prepared MFGO sample [18]. The oxygen-containing functional groups are dominated mainly by C–OH and –C–O–C– groups (single C–O bonds, see Table 1).

The composite MFGO-based membrane exhibits strong barrier properties towards permanent gases which favors its application in gas dehumidification processes (Fig. 2a). The permeability of the gases follows a tendency towards Knudsen diffusion. Typical permeability for the entire range of the studied gases does not exceed 0.0031 Barrer revealing the tight interlocking of graphene oxide nanosheets in the microstructure of MFGO ultrathin selective layer. It should be noted that the permeability of GO-based membranes strongly depends on the method of assembly of graphene oxide nanosheets. For instance, high H2-permeance was achieved in membranes obtained by spray-evaporation method resulting in GO membranes with high porosity [19]. However, common trend towards gas barrier properties is generally exhibited both by neat [20] and/or specially cross-linked/reduced graphene oxide [21], and our result stay in line with this trends.

It is remarkable, that the permeability of the composite membrane towards the studied gases has not changed with time: during 240 days, a little loss of about 2% is registered staying within the error range of gas flux measurement (Fig. 3a). The permeability of the composite membrane stands constant in time, probably, owing to small amounts of tiny packing defects inside the MFGO thin selective layer which constantly ensurre the transport of gas molecules across the membrane. It should be expected that graphene oxide nanosheets begin to shrivel due to gradual drying with time resulting in shrinkage and detachment of graphene oxide thin films from the support and should cause an increase in gas permeability. However, in our study, the employment of porous AAO supports favors the stability and constant gas permeability of MFGO-based thin film owing to cross-linking with aluminum ions and aluminol-groups on the surface of the AAO support. The structural stabilization of graphene oxide thin films with AAO supports was also evidenced in [22] and [23] for transport in liquid aqueous medium and water vapors, respectively. Therefore, the thin MFGO-based selective layer deposited on the AAO support is compact and stable in time providing constant gas barrier properties.

The game changes when we turn to the behavior of water vapors transport (Fig. 2b). The permeability of water vapors, measured in a dynamic mode, decreases rapidly within the first 30 days from membrane fresh state as the starting

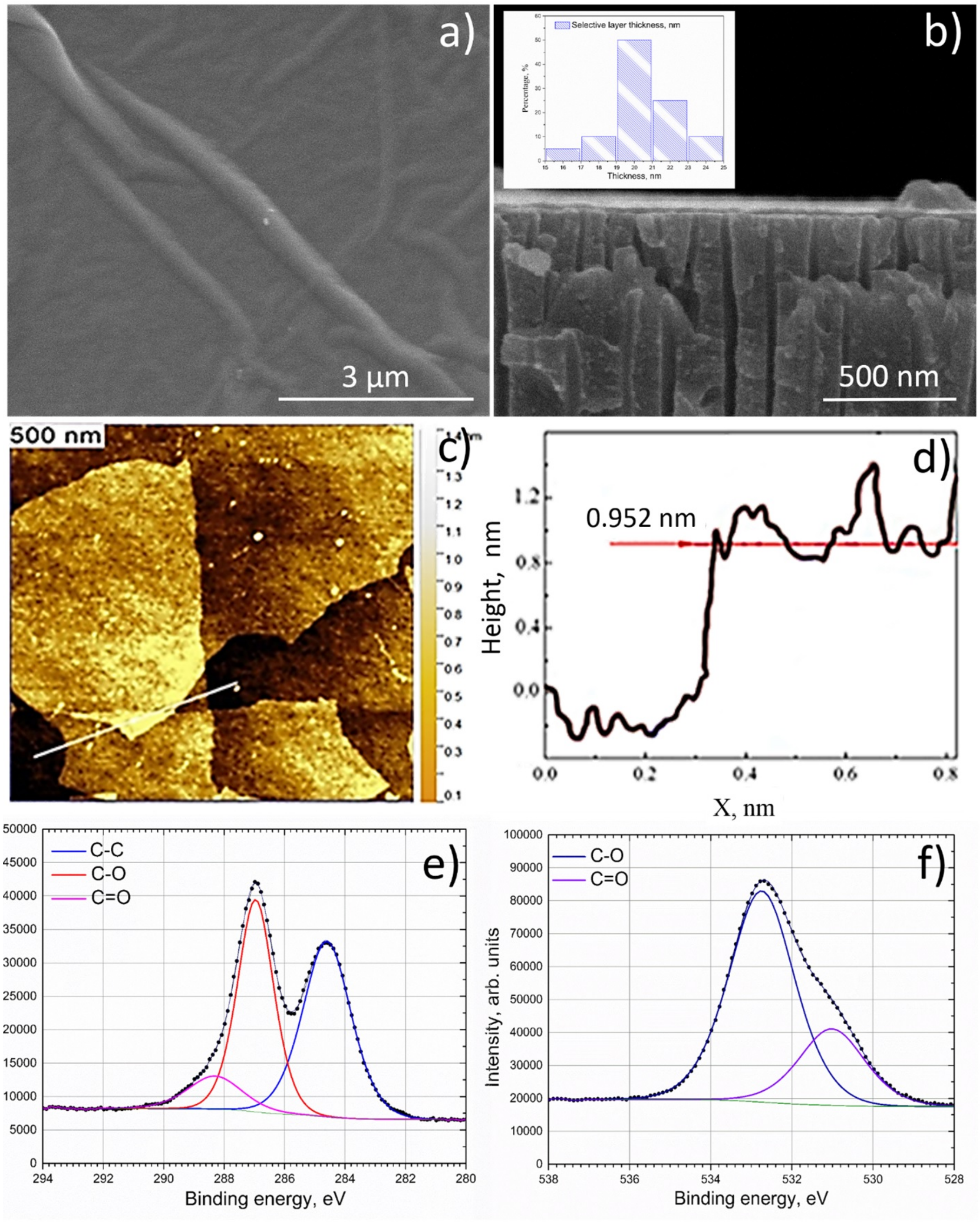

FIG. 1. a), b) SEM images of MFGO-based composite membrane: a) bottom site; b) cross-section The insert in b) shows the statistical distribution of the thickness of the MFGO-base selective layer; c), d) AFM image and height profile of MFGO nanosheets; e), f) XPS spectra fits for e) C1s and f) O1s regions for MFGO/AAO composite membrane

point. To characterize the dynamics of permeability, the coefficient of permeability loss (L_P, %) was calculated by the formula:

$$L_P = 100 \cdot \frac{P_0 - P_t}{P_0}$$

where P_0 and P_1 are permeability of the fresh membrane and the permeability of the membrane at a certain point in time (day of measurement).

According to the calculations, during the first 5 days, the membrane loses 15% of its original permeability reaching nearly 60% loss by the period of 30 days. The average daily permeability loss during the first 30 days is about 3.5% per day followed by a gradual stabilization at the level of about 0.75% per day within the remaining time up to 240 days. The rapid loss of permeability during the first month can be attributed to gradual evaporation of remaining solvent (water and methanol molecules) from interlayer galleries of the GO selective layer leading to the compaction and tightening of GO nanoflakes (particularly, the surface GO nanoflakes) until reaching some equilibrium and stable level of packing.

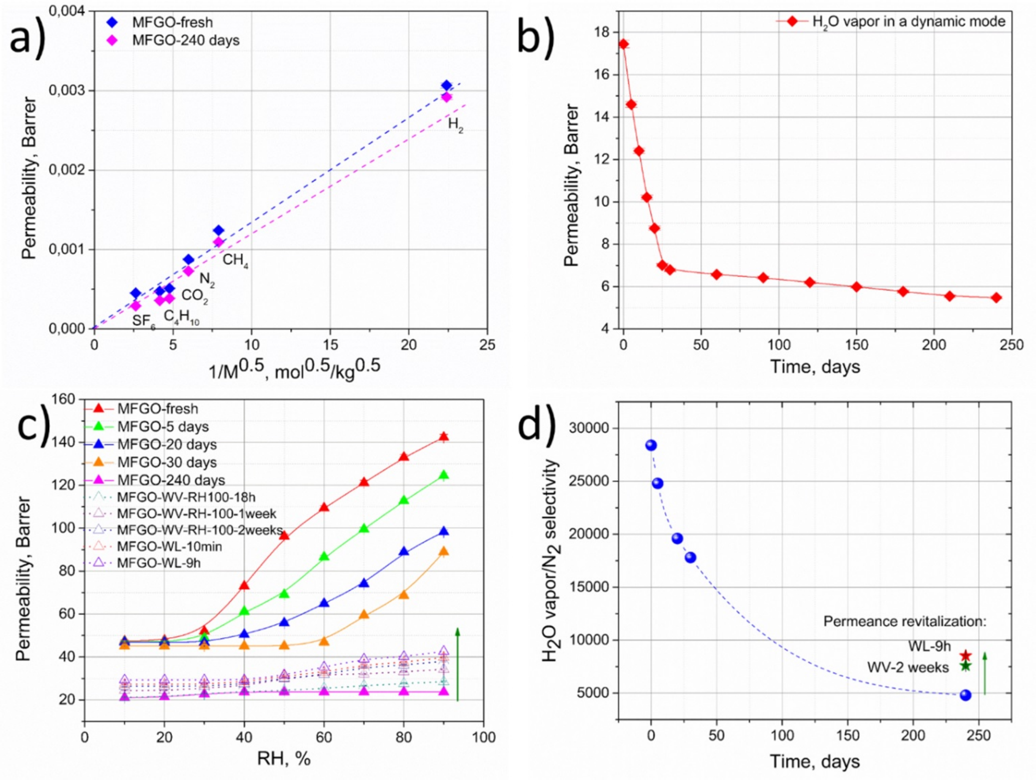

FIG. 2. Gas and vapor transport characteristics of the composite MFGO-based membrane: a) permeability towards permanent gases for MFGO freshly-prepared and aged during 240 days; b) permeability change of water vapors in a dynamic mode within 240 days; c) dynamics of RH-dependency of water vapors with time and during treatment under water vapors (WV, at RH = 100%) and liquid water (WL); d) change of water vapor-to-nitrogen selectivity with time. The restored selectivity registered under treatment with water vapors for 2 weeks (WV-2 weeks) and liquid water for 9 hours (WL-9h) is shown with green and red stars, respectively

To further understand the time-dependent water vapor transport evolution of the MFGO-based membranes, the dynamics of water vapor permeability in the entire range of relative humidity (RH) of the feed flux was measured during the 240 days. The membranes were stored in air between the measurements. According to the results (Fig. 2c), a gradual decrease in the water vapor permeability occurs in an entire range of relative humidity. It should be noted that at low relative humidity (10–30%), MFGO-based membrane reveals a relatively small permeability of about 40–50 Barrer and this range of RH of the feed stream is not valuable for practical dehumidification process. Meanwhile, a 2-fold decrease in permeability is registered even in the low-RH range after 240 days of ageing. In the middle (40–60%) and high (70–90%) RH range, an average decrease of 40% and 50% is registered, respectively, during the first 30 days reaching a 70–80% decrease within 240 days of ageing. The rapid loss of permeability during the first 30 days could be attributed to the gradual compaction of GO nanoflakes upon storage in air. In the a freshly-prepared MFGO membrane, the assembled GO nanoflakes are commonly hold in a metastable loosely-packed structure becoming compacted upon gradual evaporation of solvent molecules which are always remaining in the microstructure of as-prepared GO membranes. It is expectable that this process could mainly touch the surface sublayers of the membrane: once the solvent molecules have moved from the d-spacing of the sublayers, the entering of water molecules across the surface to the bulk of the membrane becomes restricted. The process may gradually propagate with time covering more and more GO layers of the membrane. Further decrease in water vapor permeability during more prolonged time could be caused by gradual deoxygenation of surface layers of the GO film. Obviously, the permeability of the aged GO film becomes close to that of the reduced GO [6]. The obtained results are complementary to the finding of Talyzin et al [9] who have studied the structural changes in GO during a prolonged period of time. It was shown that the GO ageing takes its origin in the process of drying and deoxygenation which starts on the surface GO nanosheets at the “GO film-air” interface and gradually penetrates deeper into the GO film.

The observed results are close to time-dependent physical ageing of some highly permeable polymers containing a large number of free diffusion volume [24, 25]. The ageing of the polymers is attributed to gradual relaxation of macromolecules from non-equilibrium conformations in freshly-prepared membranes towards stable equilibrium ones owing to a gradual evaporation of remaining solvent and thermal movement of the polymer chains. For instance, a classical polymer with intrinsic microporosity (PIM-1) reveals rapid ageing towards water vapors exhibiting permeability loss of 3–5 times in the relative humidity range of 10–70% [26]. It is remarkable that the permeability of the polymers can be partially revitalized by treatment with low-molecular alcohols (particularly, methanol) [17,26], however, within several weeks after the treatment, the polymer again inevitably loses its permeability. To check the possibility of revitalizing the GO permeability after ageing, the membrane was subjected to water vapors treatment under RH =100% in a desiccator during 18 h, 1 and 2 weeks. It was revealed that the treatment of the membrane during 2 weeks allows one to restore water permeability by only 20 and 40% from the aged state in the low/middle and high RH range of the feed stream. Next, the membrane was soaked in liquid water for 10 min, 3 and 9 hours. However, even after treatment with liquid water, the maximum level of permeability restoration of 40% from the aged state for high RH-levels of feed stream was achieved (Fig. 3c). The observed results indirectly show that the decrease in water vapor permeability is caused not only by gradual drying of GO-thin film but also by partial deoxygenation of surface sublayers of the GO membrane which strongly restrict the diffusion of water molecules into the bulk of the membrane. A decrease in water vapor transport significantly affect the H2O/N2 selectivity: a nearly 6-fold decrease of this membrane characteristic is observed (Fig. 3d).

The obtained results show that GO-based thin films can dramatically lose their permeability towards water vapors and, moreover, the aged membranes cannot be revitalized by treatment with water neither in the form of vapors nor liquid. It should be noted, that these conclusions could be applied only towards thin GO films (20 nm), whereas for thicker films (in micrometer range), other ageing behavior could be registered and further experiments are required. Moreover, the use of water-methanol suspension and large size of GO nanoflakes (750±100 nm) also could favor the ageing process. Thus, to consider GO-based membranes, particularly, in the form of thin films, for industrial application, it is of high importance to develop standards for the conditions of the membrane storage and special modifications to prevent ageing effects.

Generally, whereas, the impact of ageing of polymers on the permeability of gas and vapors components is studied well enough [8], the long-term permeability dynamics of not only GO, but other 2D materials-based membranes in time suffers from the lack of attention. At present, the so called phenomenon of wetting ageing of 2D-materials is generally considered [27], and, coupled with long-term measurements of membrane transport characteristics it could give a complete information for a reliable design not only for membranes but also for membrane catalysts, sensors and elements for energy storage devices.

4. Conclusions

The ageing of thin GO-based membranes during storage under ambient conditions don't cause any significant changes in permanent gas transport, but induces a strong decrease in water vapors permeability. Gradual structural compaction caused by drying of GO at ambient conditions results in a decline of GO film permeability, particularly, during the first 30 days of storage (with the average permeability loss coefficient of 50–60%) and lost of 80% of initial permeability along the period 240 days. Treatment of the aged membrane under saturated water vapors for 2 weeks as well as soaking in liquid water for 9 h allowed one to achieve 40% restoration of the membrane permeability from the aged state at high RH of the feed stream. Thus, it is highly recommended to store freshly-prepared GO-based membranes under saturated water-vapor environment (for instance, in a desiccator with 100% RH of water vapors) to preserve the original permeability of the membranes.

Ageing of GO membranes can dramatically hinder their performance and should inevitably be taken into consideration for the design of GO-based membranes as well as other devices employing graphene oxide films as a working material. Further experiments are required concerning the influence of long-term ageing on the performance of GO-membranes with different thickness, C/O ratio and deposited from various solvents. Moreover, the rational search and design of different types of spacers and modifying agents preventing the GO nanoflakes compaction as well as deoxygenation during ageing is of high demand.

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Information about the authors:

Ekaterina A. Chernova – Lomonosov Moscow State University, Faculty of Materials Science, 119991, Moscow, GSP-1, 1-73 Leninskiye Gory, Russia; chernova.msu@gmail.com

Konstantin E. Gurianov – Lomonosov Moscow State University, Faculty of Materials Science, 119991, Moscow, GSP-1, 1-73 Leninskiye Gory, Russia; gurianovke@yandex.ru

Mikhail V. Berekchiian – Lomonosov Moscow State University, Faculty of Materials Science, 119991, Moscow, GSP-1, 1-73 Leninskiye Gory, Russia; mikhail.berekchiyan@yandex.ru

Victor A. Brotsman – Lomonosov Moscow State University, Faculty of Chemistry, 119991, Moscow, GSP-1, 1-3 Leninskiye Gory, Russia; brotsman_va@mail.ru

Rishat G. Valeev – Udmurt Federal Research Center of the Ural Brunch of Russian Academy of Sciences (UdmFRC of UB RAS), Izhevsk, st. them. Tatiana Baramzina 34, 426067, Russia; rishatvaleev@mail.ru

Olesya O. Kapitanova – Lomonosov Moscow State University, Faculty of Chemistry, 119991, Moscow, GSP-1, 1-3 Leninskiye Gory, Russia; olesya.kapitanova@gmail.com

Alina V. Kirianova – Lomonosov Moscow State University, Faculty of Materials Science, 119991, Moscow, GSP-1, 1-73 Leninskiye Gory, Russia; vov-lena2010@yandex.ru

Alexey V. Lukashin – Lomonosov Moscow State University, Faculty of Materials Science, 119991, Moscow, GSP-1, 1-73 Leninskiye Gory, Russia; alexey.lukashin@gmail.com

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