ChemComm

Graphene Oxide Membranes with Narrow Inter-Sheet Galleries for Enhanced Hydrogen Separation

Journal:	*ChemComm*
Manuscript ID	CC-COM-12-2018-010283.R1
Article Type:	Communication

Journal Name

COMMUNICATION

Graphene Oxide Membranes with Narrow Inter-Sheet Galleries for Enhanced Hydrogen Separation

Amr F. M. Ibrahim[a,b], Fateme Banihashemi[b], Y.S. Lin[b]*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

This paper reports synthesis of graphene oxide (GO) membranes with narrow interlayer free spacing on scalable polyester substrates using GO sheets prepared by Brodie's method. The GO membranes show interlayer free spacing of ~0.32 nm with significantly improved hydrogen perm-selectivity than the GO membranes with the large inter-sheet spacing reported in the literature.

Graphene oxide (GO) nanosheets offer an exciting opportunity to assemble membranes with distinct laminar structure for gas separation.[1] Recently, many studies reported synthesis of GO membranes formed by stacking GO sheets, prepared using modified Hummers' method, for hydrogen separation. These GO membranes showed great variations in hydrogen separation characteristics (for example, H_2/CO_2 selectivity is 3400, [2] 240, [3] 20.9, [4] 30, [5] 30, [6] 22, [7] 10, [8] and 3.5 [9]). It is recognized [10, 11] that GO membranes show inter-sheet and intra-sheet pathways for gas permeation. The inter-sheet pathways represent the interlayer spacing between stacked GO sheets and channels formed at membrane wrinkles, while intra-sheet pathways are formed by the structural defects within GO sheets. In recent studies, [7, 12] we found that large gas molecules (CH_4, N_2 and CO_2) flow with Knudsen like permeation characteristics, dominantly through GO inter-sheet pathways. Small gas molecules (H_2 and He) permeate through both inter-sheet and intra-sheet pathways. In both studies on GO membranes showing high H_2 selectivity, [2, 3] the GO sheets obtained from commercial sources were used to form GO membranes on commercial anodic aluminum oxide substrates, and the GO membranes were very thin (≤ 20 nm). It is likely that gas permeation through GO membranes prepared in these studies was dominated by transport through highly selective small inter-sheet defects.

The defect size and concentration on GO sheets depend on GO sheet synthesis method and process conditions, and are very difficult to control.[13] This explains few follow-up reports showing such highly hydrogen-selective GO membranes. Several research groups reported GO membranes with relatively low but consistent hydrogen selectivity, [4-9] and these GO membranes were prepared from home-made GO sheets synthesized by the Hummers' method (referred to as Hummers GO sheets or GO-H). In these GO membranes the gas transport through the inter-sheet space is the likely dominating mechanism. The size of the interlayer spacing, which can be estimated by XRD, determines the diffusion-controlled selectivity. [14] It is more desirable to prepare GO membranes with reduced size of the inter-sheet space to improve the hydrogen selectivity of GO membrane to ensure controlled pore size and reproducibility of membrane synthesis. Several efforts were reported to reduce the size of the inter-sheet spacing of GO-H membranes by methods such as cross-linking, [15] alternative deposition of polyethyleneimine / GO layers, [5] using slow rate vacuum filtration [9] or applying pressurized filtration [16], but all failed to modulate the size of the interlayer spacing of staked GO sheets to smaller than 4 Å. Thus, selectivity of these GO membranes remained low. Here, we report a new method to prepare GO membranes with significantly reduced size of the interlayer spacing (~ 3.2 Å) using GO sheets prepared by a modified Brodie's method.[17] The prepared membranes show consistently improved hydrogen molecular sieving properties compared with GO membranes from Hummers' GO sheets in our previous publication. [7]

In a typical procedure, GO sheets were prepared from graphite by a modified version of Brodie's method [17] (referred to here as Brodie GO sheets, or GO-B) and GO membranes were prepared on top of scalable macroporous polyester track etch substrates by vacuum filtration. The average size of Brodie and Hummers GO sheets is respectively about 3.5 µm and 30 µm as determined by SEM (Fig. S1, ESI). The FTIR spectrum for GO-B sheets is quite similar to that for the GO-H sheets (Fig. S2). They exhibit the same peaks, with difference in relative intensity of

[a] Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt.
[b] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA.
* Corresponding author email: Jerry.lin@asu.edu

the adsorption bands at 1369, 1725 and 1222 cm^{-1} assigned respectively for C-OH, C=O and C-O bonds. This shows that Hummers' and Brodie's synthesis methods indeed result in different chemical functionalities of GO. XRD patterns given in Fig. 1-A shows graphene structure of the GO sheets in comparison with graphite. The d-spacing increases from 3.34 Å for graphite to 6.0 and 8.5 Å for GO-B and GO-H respectively. The Raman spectra for the GO-B and GO-H powder (Fig. S3) show the well-known Raman characteristics of carbon materials, the G band at 1580 cm^{-1} and D band at 1350 cm^{-1}, assigned to the graphitized structure and local defects/disorder. [18] Using the method of Cançado and coworkers [19] the defect density is found to be the same for GO-B and GO-H (0.16 per nm^2)(see ESI for details). The SEM images of the surface and cross sections of the synthesized GO-B and GO-H membranes are given in Fig. 1-C&D. The thickness of the GO membranes is about 200 nm. Overall, the surface is relatively corrugated, showing sheet edges and extrinsic wrinkles with no obvious macroscopic defects (pores or cracks). XRD patterns of the Brodie and Hummers GO membranes are similar to those of GO powder samples, except for the peak of polyester substrate. The corresponding d-spacing using Bragg's law is 6.5 and 8.6 Å for the Brodie and Hummers GO membranes. The slight variation of d-spacing between the powder and the membranes is due to the formation of wrinkles and sodium ions intercalation (added as NaOH during sonication of GO-B sheets). Considering the ~3.34 Å electronic clouds around graphene sheets, the interlayer spacing heights for GO-B and GO-H membranes are respectively 3.2 and 5.3 Å. [19]

The gas perm-selectivity and transport behavior of GO membranes synthesized in this work were investigated by measuring the permeability and selectivity of single gases: H_2, He, CH_4, N_2 and CO_2 first, and then of H_2/CO_2 binary mixture. A notable reduction in the pure permeability of GO-B membrane was noticed compared to GO-H membrane as given in Table 1. The permeability ratio for different gases for GO-H over GO-B shows a significant reduction in the permeability of large gas molecules (N_2, CH_4, and CO_2) compared to the reduction in the permeability of small gas molecules (H_2 and He) for GO-B membrane. As a result, the pure gas selectivity of hydrogen over large gas molecules has increased about twice compared to the selectivity of GO-H membrane as given in Table 1. The inter-sheet and intra-sheet gas transport model proposed in our previous publications [7, 12] can be used to discuss the permeation and separation data obtained in this work. Basically, the reduction in the height of the free space between stacked GO-B sheets to 3.2 Å results in increasing the activation energy for diffusion, E_d, for large gas molecules and add more restriction to their flow in inter-sheet pathways. The spacing height is now smaller than the size of the propping large gas molecules (CH_4 N_2 and CO_2) and thus no permeance for these molecules should be expected in the interlayer space of stacked sheets. However, if extrinsic wrinkles exist as observed in SEM surface images in Fig. 1-C, the height of channels formed at membrane wrinkles is ~1-2 times the free interlayer space detected by XRD [12] and thus, these channels could still allow minimal flow of tested large molecules.

The reduction in the permeability of small gas molecules for GO-B compared to GO-H membrane results significantly from a permeability reduction through GO sheet defects. The distance between point-like defects, L_D determined by Raman is about 1.39 and 1.40 nm for GO-B and GO-H respectively. The tortuosity factor in defect pathways is determined by (L_D/d) and thus $\tau_{GO\text{-}H}/\tau_{GO\text{-}B}$=0.6, which suggests a reduction in the permeability of small gas molecules through the intra-sheet pathway for GO-B membranes by 1.65 compared to GO-H membranes. The reduction in the permeability of GO-B compared to GO-H for small gas molecules is ~2.8.

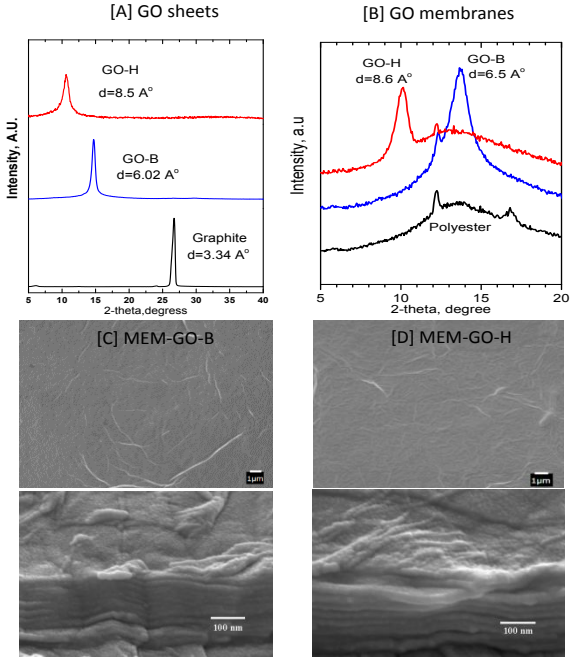

Fig. 1. Characteristics of GO sheets and membranes: [A] XRD patterns of GO sheets, [B] XRD patterns of GO membranes [C, D] SEM images of GO-B and GO-H membranes.

Table 1 Pure gas permeability of GO-B membrane compared to that of GO-H membrane from our previous publication [7]

Gas type	Mw. [g/mol]	kinetic diameter, Å	Permeability, Barrer			Selectivity (H_2/gas_i)	
			GO-H	GO-B	GO-H/GO-B	GO-H	GO-B
H_2	2	2.9	79.71	28.26	2.82		
He	4	2.6	61.50	21.74	2.83	1.30	1.30
CH_4	16	3.8	5.07	1.02	4.97	15.72	27.71
N_2	28	3.6	2.53	0.47	5.38	31.51	60.13
CO_2	44	3.3	2.26	0.35	6.40	35.27	80.74

1 Barrer = 1 × 10^{-10} cm^3 cm/cm^2·sec·cm Hg at STP

Pure H_2 permeability of polyester support at same permeation conditions is 2x 10^{-6} mol/(m^2spa) , ~59710 Barrer and H_2/CO_2 selectivity is 3.3.

Journal Name

COMMUNICATION

The interlayer spacing in GO-H membranes is larger than that of GO-B membrane, which makes the diffusion of small gas molecules from one defect to another between stacked GO sheets in case of GO-B membranes difficult. This causes more reduction in the permeability of small gas molecules in intra-sheet pathways.

The GO-B membrane is perm-selective to H_2 with pure and H_2/CO_2 mixture (50/50 vol%) gas feeds. The binary mixture gives slightly lower, ~20% H_2 permeability and the increased CO_2 permeability causes a reduced H_2/CO_2 selectivity (from 80.7 to 50.0) in H_2/CO_2 mixture similar to GO-H, where selectivity decrease from 35.3 in pure gas feeds to 22.0 in mixture. [7] A controlled H_2/CO_2 mixture experiment for the polyester support show a H_2/CO_2 separation factor of 3.

Table 1 shows effectiveness to improve gas selectivity by reducing the size of inter-sheet spacing. Furthermore, XRD results given in Fig. S4 indicate an enhancement of the packing and stacking density of GO-B sheets as a function of applied filtration pressure. The GO peak becomes more intense and shifts to a larger 2θ angle when pressure is applied in the filtration system. When the applied filtration pressure is 2 bar, the GO-B membrane shows a diffraction peak at 2θ of 14.1° corresponding to a free inter-sheet space of 3 Å [19]. This effect of the applied filtration pressure on the reduction of the inter-sheet space was also found on the Hummers derived GO membranes by other researchers[16, 20]. The Brodie-derived GO membrane, prepared with 2 bar filtration pressure difference, exhibit superb separation characteristics, with H_2/CO_2 mixture separation factor of 214, H_2 permeance of 2.9 x 10^{-8} mol/(m^2.s.Pa) and confirmed operation stability for 36 h as shown in Fig. S6-A. H_2/CO_2 separation factor decreases with increasing temperature (Fig. S6-B), suggesting a more activated CO_2 diffusion than that of H_2 through GO membranes, resulting from the tight fit of CO_2 molecules in GO-B sheet defects. [2, 3, 7]

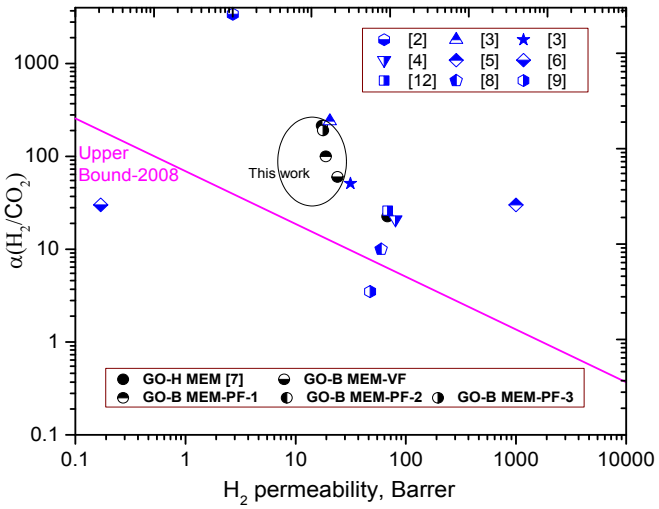

Fig. 2. H_2/CO_2 equimolar mixture separation performance of GO-B membranes prepared in this work by vacuum (VF) and pressurized (PF) filtration at pressures of 1, 2, 3 bar compared with the 2008 upper bound of the polymeric membrane [20] and other previous GO membrane studies.

This separation performance has exceeded the upper bound of reported polymeric membranes [21] and show superior, reproducible separation performance compared with previous laminar GO membrane studies as presented in Fig. 2. Our results idicate that GO-B can give consistently high selectivity than most GO membrane works, and comparable to Zhao's GO membranes [3] on 20 nm non-scalable anodic alumium oxide disks, which in turns will open up future oportunities for potential enhanced membrane peremeace with thinner GO-B membranes.

In summary, GO membranes with reduced interlayer spacing of about 0.32 nm can be prepared using Bodiede drived GO sheets on polyester substrates by filtration. The GO membranes prepared by Brodie's method show significantly improved separation properties compared to the GO membranes formed using the Hummers' derived GO sheets with a similar sheet defect density. Reducing the interlayer free spacing height results in more reduction in the permeability of large gas molecules (CH_4, N_2 and CO_2) than the small gas molecules (H_2 and He) leading to the improved selectivity for H_2 over large gas molecules. This synthesis method offers high reproducibility in controlling separation characteristics of GO membranes which is important to their scaling up for industrail applications.

References

1 H. Huang, Y. Ying and X. Peng, *J. Mater. Chem. A*, 2014, **2**, 13772-13782.

2 H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, H. J. Ploehn, Y. Bao and M. Yu, *Sci.*, 2013, **342**, 95-98.
3 C. Chi, X. Wang, Y. Peng, Y. Qian, Z. Hu, J. Dong and D. Zhao, *Chem. Mater.*, 2016, **28**, 2921-2927.
4 K. Guan, J. Shen, G. Liu, J. Zhao, H. Zhou and W. Jin, *Sep. Purif. Technol.*, 2017, **174**, 126-135.
5 J. Shen, G. Liu, K. Huang, Z. Chu, W. Jin and N. Xu, *ACS nano*, 2016, **10**, 3398-3409.
6 H. W. Kim, H. W. Yoon, S.-M. Yoon, B. M. Yoo, B. K. Ahn, Y. H. Cho, H. J. Shin, H. Yang, U. Paik, S. Kwon, J.-Y. Choi and H. B. Park, *Sci.*, 2013, **342**, 91-95.
7 A. Ibrahim and Y. S. Lin, *J. Membr.Sci.* 2018, **550**, 238-245.
8 K. Huang, J. Yuan, G. Shen, G. Liu and W. Jin, *Chin. J.Chem. Eng.*, 2017, **25**, 752-759.
9 G. Romanos, L. M. Pastrana-Martínez, T. Tsoufis, C. Athanasekou, E. Galata, F. Katsaros, E. Favvas, K. G. Beltsios, E. Siranidi, P. Falaras, V. Psycharis and A. M. T. Silva, *J. Membr. Sci.*, 2015, **493**, 734-747.
10 L. Huang, M. Zhang, C. Li and G. Shi, *J. Phys.Chem. Lett.*, 2015, **6**, 2806-2815.
11 J. Lyu, X. Wen, U. Kumar, Y. You, V. Chen and R. K. Joshi, *RSC Adv.*, 2018, **8**, 23130-23151.
12 A. Ibrahim and Y. S. Lin, *Chem. Eng. Sci.*, 2018, **190**, 312-319.
13 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS nano*, 2010, **4**, 4806-4814.
14 R. K. Joshi, P. Carbone, F. C. Wang, V. G. Kravets, Y. Su, I. V. Grigorieva, H. A. Wu, A. K. Geim and R. R. Nair, *Sci.*, 2014, **343**, 752-754.
15 W.-S. Hung, C.-H. Tsou, M. De Guzman, Q.-F. An, Y.-L. Liu, Y.-M. Zhang, C.-C. Hu, K.-R. Lee and J.-Y. Lai, *Chem. Mater.*, 2014, **26**, 2983-2990.
16 C.-H. Tsou, Q.-F. An, S.-C. Lo, M. De Guzman, W.-S. Hung, C.-C. Hu, K.-R. Lee and J.-Y. Lai, *J. Membr. Sci.*, 2015, **477**, 93-100.
17 B. C. Brodie, *Philos. Trans. R. Soc. of London*, 1859, **149**, 249-259.
18 R. Vidano and D. Fischbach, *J.Am. Ceram. Soc.*, 1978, **61**, 13-17.
19 L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, 2011, **11**, 3190-3196.
20 Y. P. Tang, D. R. Paul and T. S. Chung, *J. Membr. Sci.*, 2014, **458**, 199-208.
21 L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390-400.

Table of contents

- Brodie's GO sheets are prepared, characterized and compared to Hummers' GO sheets.
- GO-B membranes are synthesized on polyester substrates using filtration.
- Permeability reduction of large gas molecules (CH_4, N_2 and CO_2) is more significant compared to permeability reduction of small gas molecules (H_2 and He).
- Pressure filtration enhances the packing density of GO-B sheets

Keyword: graphene oxide membrane, narrow interlayer galleries, H_2/CO_2 mixture separation, Brodie and Hummers methods.