17th International Conference on Inorganic Membranes
New Frontiers for Inorganic Membranes
July 1 - 5, 2024
Oceania Convention Center - Florianópolis - Brasil

Graphene Oxide Membrane Deposited on Alumina Hollow Fiber Substrate for Hydrogen Separation

G. G. Ascendino [a*], K. R. Dorneles [a], W. A. Dias [a], M. H. M. Reis [a] and C. E. Hori [a]
[a] Department of Chemical Engineering, Federal University of Uberlândia, Uberlândia, Brazil
[*] guilherme.ascendino@gmail.com

Introduction

Hydrogen (H_2) has been considered to replace fossil fuels as an energy vector because of its high energy density and being water the only by-product from its combustion. Typically, H_2 is produced by steam methane reforming or biomass and gasification, which involve the production of a gas mixture. Membrane separation processes are currently suggested to separate gas mixtures with high efficiency and low energy demand [1]. Graphene oxide (GO) material presents favorable characteristics for the development of membranes with appropriate gas selectivity and permeability [1-4]. The choice of proper substrates is another key point to be considered in the development of composite GO membranes for gas separations. The substrates should present high porosity to not imply the permeating flux and a smooth surface for the deposition of a uniform thin GO layer [5].

In this work, asymmetric alumina (Al_2O_3) hollow fiber was produced and used as support for the deposition of GO by the vacuum-assisted dip-coating method. Then, the gas permeation and selectivity for the GO membrane were evaluated for hydrogen (H_2), nitrogen (N_2), and carbon dioxide (CO_2).

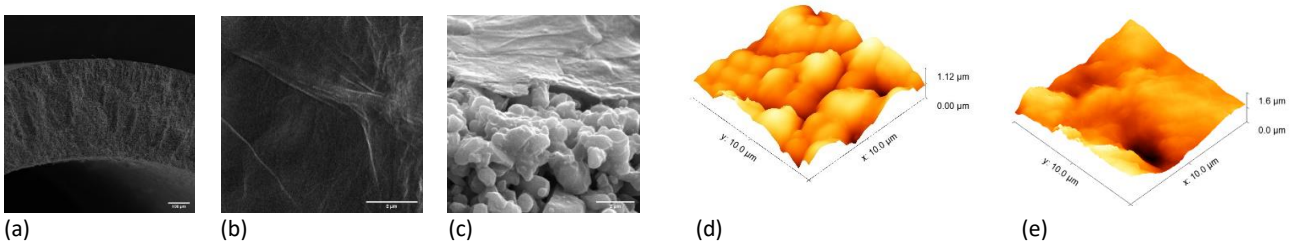
Material and Methods

Graphene oxide was synthesized by the modified Hummers method [3]. The Al_2O_3 hollow fiber substrates were produced by the phase inversion method [5]. The ceramic dispersion was composed of 58.0 wt% of ceramic powder (Al_2O_3, α-phase, 99.9% of purity, Alfa Aeser), 36.1 wt% of dimethyl sulfoxide (DMSO, Vetec, Brazil), 5.5 wt% of polyethersulfone (PES, Veradel 3600P, Solvay) and 0.4 wt% of polyvinylpyrrolidone (PVP, Sigma Aldrich). After the phase inversion, the substrates were dried at room temperature for 24 h and then sintered in a tubular furnace (Carbolite, model TZF 16/610) to a target temperature of 1400 °C. Then, the Al_2O_3 hollow fibers were immersed for 24 h in a dopamine solution (0.01 mol L^{-1}) composed of dopamine hydrochloride (Sigma Aldrich), tris(hydroxymethyl)aminomethane (PA, Dinamica, Brazil), and hydrochloric acid (HCl, 98%, Exodus, Brazil) to improve the GO adherence on the substrate surface. Before GO deposition on the substrates, the dopamine excess was removed with ultrapure water (Milli-Q®).

A GO suspension was prepared at a concentration of 1.0 mg mL^{-1} and exfoliated in an ultrasonic bath (Sonic Mill, 1790 W, 20 kHz) for 30 min. Then, the suspension was centrifuged (Thermo Scientific, Heraeus Megafuge 8) at 5000 rpm for 40 min. The GO membranes were deposited on the hollow fiber outer surfaces by the vacuum-assisted dip-coating method [3]. After the deposition, the as-prepared GO membranes were dried in an oven at 80 °C for 3 h. Then, a single as-prepared membrane was placed in a stainless-steel tube with Araldite® epoxy glue to start the gas permeation experiments at room temperature. Hydrogen (H_2), nitrogen (N_2), and carbon dioxide (CO_2) were the permeated gases, and each gas was fed on the fiber shell side and the permeate was fluxed from the lumen side. The transmembrane pressure was varied from 2.0 to 10.0 kPa and the permeate volume was measured using a bubble flow meter. The membranes were characterized according to Scanning Electron Microscopy (SEM, Tescan, VEGA 3 LMU model). Furthermore, the average roughness of the Al_2O_3 hollow fiber before and after the GO deposition was analyzed by Atomic Force Microscopy (AFM, Shimadzu, model SPM-9600).

Results and Discussion

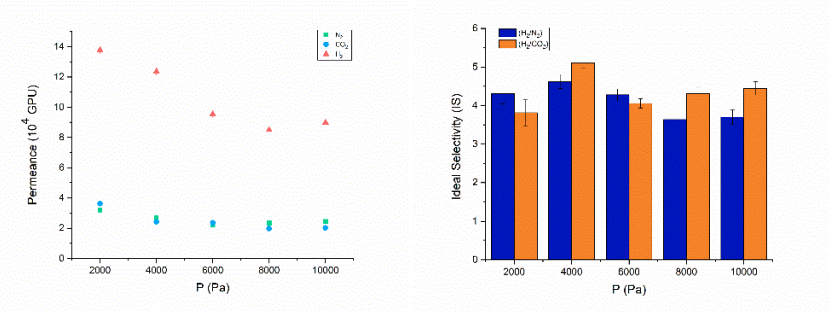
Fig. 1a shows the SEM image of the Al_2O_3 hollow fiber, indicating an asymmetric pore size distribution with microchannels across its structure. The micro-channels ensure high gas permeations through the substrate [3]. The synthesized GO showed an aspect of crumbled sheets (Fig. 1b), which is associated with the presence of oxygen functional groups in the GO structure [3]. Fig. 1c presents the SEM image of Al_2O_3 hollow fiber after the GO deposition, indicating that the GO membrane formed a homogeneous layer with a wrinkled aspect. Furthermore, Fig. 1d and Fig. 1e present the AFM image of the Al_2O_3 hollow fiber before and after GO deposition, respectively. The surface average roughness of the Al_2O_3 hollow fiber outer surface was 120.1 ± 5.2 nm before the GO deposition and 78.5 ± 3.6 nm after the GO deposition.



(a) (b) (c) (d) (e)

Fig. 1 – (a) SEM image of the Al_2O_3 hollow fiber, (b) SEM image of the GO suspension, (c) cross-section SEM image of the Al_2O_3 hollow fiber after GO deposition, (d) AFM image of the Al_2O_3 hollow fiber before GO deposition and (e) AFM image of the Al_2O_3 hollow fiber after GO deposition.

Fig. 2a shows the permeances of H_2, CO_2, and N_2 at transmembrane pressures from 2.0 to 10.0 kPa. The H_2 permeance through the GO membrane was higher than the N_2 and CO_2 permeance values because the H_2 has the lowest kinetic diameter. The lowest permeance values were: 22,300 GPU for N_2, 19,700 GPU for CO_2, and 85,000 GPU for H_2. As indicated in Fig. 2b, the highest H_2/N_2 and H_2/CO_2 selectivity values were 4.62 ± 0.18 and 5.10 ± 0.12 respectively. Ribeiro et al. [3] deposited a GO membrane layer on spinel hollow fibers and the membrane exhibited H_2 permeance of 2,450 GPU and H2/N2 selectivity of 3.5. Zhang et al. [4] proposed the controlling of the interlayer spacing of the GO sheets by the thermal reduction process at moderate temperatures and the produced quasi-reduced GO membrane presented an H_2 permeance of 780 GPU and the highest H_2/CO_2 selectivity reported to date (3636 ± 312). Thus, the GO membrane produced in this work probably presented some structural defects that increased the gas permeance and decreased the selectivity.



(a) (b)

Fig. 2 – (a) Gas permeances through the GO membrane and (b) the ideal selectivities for gas permeations through the GO membrane.

Conclusions

The GO deposition on the Al_2O_3 hollow fiber support was done by vacuum filtration, ensuring the uniform stacking of a GO layer on the substrate. The prepared membrane presented higher H_2 permeances than CO_2 and N_2 permeances, but the membrane structure should be improved to increase its selectivity.

References

[1] Chuah, C. Y., Lee, J. and Bae, T.-H., "Graphene-based Membranes for H_2 Separation: Recent Progress and Future Perspective," Membranes, 10(11), 336 (2020).
[2] Liu, C., Zhang, X., Zhai, J., Li, X., Guo, X. and He, G., "Research progress and prospects on hydrogen separation membranes," Clean Energy, 7, 217-241 (2023).
[3] Ribeiro, S. R. F. L., Bessa, L. P., Cardoso, V. L. and Reis, M. H. M., "Enhanced hydrogen permeance through graphene oxide membrane deposited on asymmetric spinel hollow fiber substrate," International Journal of Hydrogen Energy, 47, 9616-9626 (2022).
[4] Zhang, X., Wang, N., Liu, T., Wu, Y., Wang, Z. and Wang, H., "Precisely tailored graphene oxide membranes on glass fiber support for efficient hydrogen separation," Journal of Membrane Science, 675, 121529 (2023).
[5] Terra, N. M., Lemos, C. O. T., da Silva, F. B., Cardoso, V. L. and Reis, M. H. M., "Characterisation of asymmetric alumina hollow fibres: application for hydrogen permeation in composite membranes," Brazilian Journal of Chemical Engineering, 33 (3), 567-576 (2016).