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

Supported Carbon Membrane Derived from Poly(Ether Imide) and Polyaniline for O_2/N_2 Separation

R. A. Serpa*, R. V. Gonçalves, L. K. Schindel, L. D. Pollo
Department of Chemical Engineering, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil
* raissaserpa14@gmail.com

Abstract

The production of oxygen from air separation plays a crucial role in various industries, enabling the effective and safe utilization of these gases in different applications, including the medical, electronics, and semiconductor fields. Traditional gas separation methods exhibit high energy consumption. The development of supported carbon membranes (SCMs) aims to address this problem. In this study, the strategy for enhancing the transport properties of SCMs was to incorporate polyaniline (PAni) into the precursor polymer poly(ether imide) (PEI).

PAni was synthesized in the form of emeraldine salt using hydrochloric acid and ammonium persulfate as the primary dopant and oxidizing agent, respectively. Subsequently, PAni was added to the precursor polymer solution of PEI and N-methyl-2-pyrrolidone, under magnetic stirring, and dispersed in the solution using tip sonication. To enhance the mechanical stability of these membranes, flat alumina supports were produced using the dry pressing methodology, and subsequently sintered up to a maximum temperature of 1400 °C. Then, the PEI/PAni precursor dispersion was applied onto the surface of a flat alumina support using the spin coating method. Three coatings were performed. The resulting supported membrane was subjected to pyrolysis in a heating protocol with a maximum temperature of 450 °C, under an inert nitrogen atmosphere. For comparison purposes, a PEI-based SCM was prepared. The morphology of the samples were characterized by scanning electron microscopy (SEM), the surface area by N_2 sorption and desorption employing the Brunauer, Emmett, and Teller (BET) model, and the performance through the permeation of pure gases (O_2 and N_2) at room temperature.

As can be seen in Fig. 1, SEM images revealed efficient synthesis of PAni fibers [1]. The formation of a homogeneous and defect-free carbon selective layer derived from PEI/PAni, adequately adhered to the alumina support, was observed.

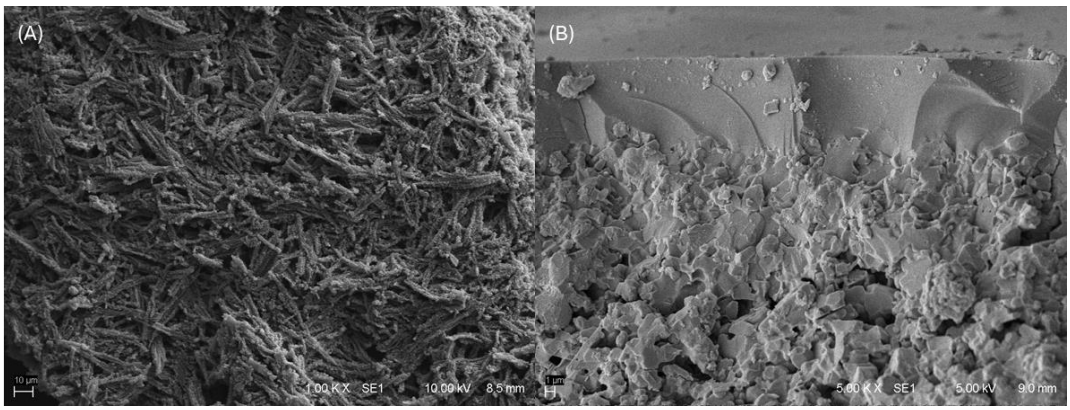

Fig. 1 – SEM images of (A) PAni fibers and (B) supported carbon membrane of PEI/PAni

On Fig. 2, can be observed that a low amount of nitrogen was adsorbed by the samples during analysis compared to what would be expected for other inorganic samples, such as zeolites and ceramics [2]. The low pyrolysis temperature used promoted incomplete degradation of the material, leading to the presence of residual functional groups and preserving characteristics of the polymeric precursors. The addition of PAni to the samples increased the porosity of the formed carbon matrix, evidenced by the higher volume of adsorbed gas and the presence of an H4-type hysteresis characteristic of materials with slit-like pores. Furthermore, the hysteresis at low pressures indicates an irreversible adsorption phenomenon of the probe molecules in the smaller diameter pores [3]. The negative values of adsorbed gas volume observed for the CMPEI, CMPP-0.1, and CMPP-0.5 samples are attributed to inherent analytical errors of the analysis, since the samples exhibit low N_2 adsorption. A higher fraction of pores can be observed, for all samples, at approximately 6 Å, indicating the formation of a microporous material. The addition of PAni promoted an increase in this microporosity, increasing the fraction of pores with a 6 Å diameter with the increase in PAni content. Smaller

diameters could not be computed by the analysis, given that the probe molecule, nitrogen, has a kinetic diameter of 3.64 Å, making it unable to access pores of smaller diameter.

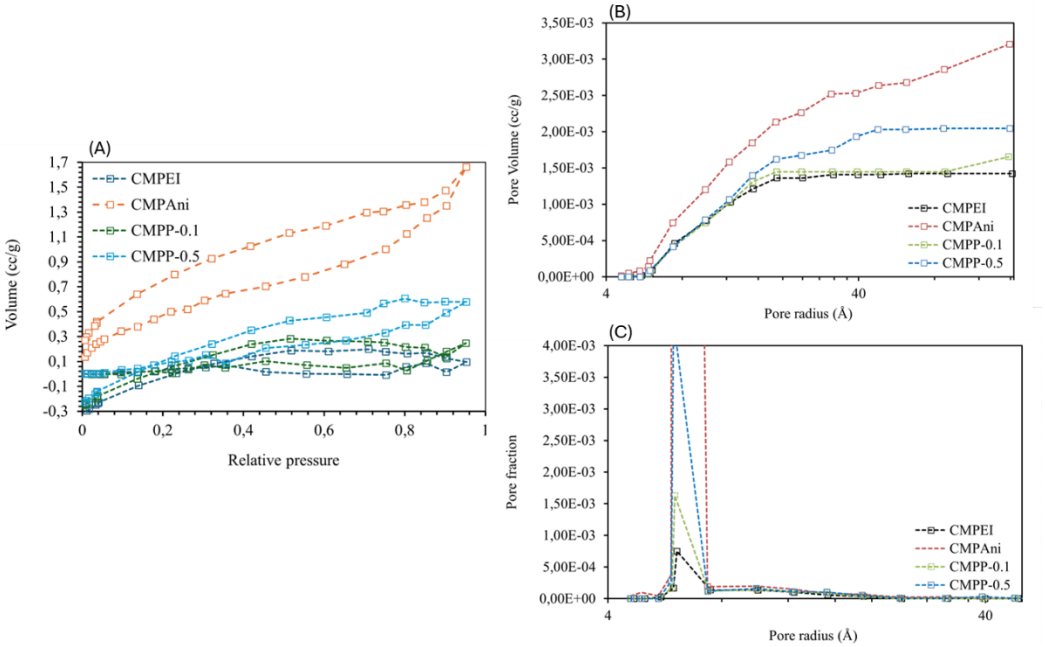

Fig. 2 – (A) Sorption and desorption N_2 isotherms at 77 K, (B) pore volume and (C) pore sizes distribution for CMPEI, CMPANI, CMPP-0.1 and CMPP-0.5

Preliminary performance tests showed that incorporating PAni into the precursor solution led to an increase in O_2 gas permeability and a decrease in N_2 permeability, resulting in enhanced ideal selectivity for the gas pair under analysis. According to Gupta, Hellgardt and Wakeman [4], this result can be justified by the interaction between O_2 gas and the polaron present in the nitrogen atom of doped PAni. Additionally, benzene rings can provide a high electron density, hindering the transport of gases such as N_2. These results demonstrate the potential application of the PEI/PAni-derived SCM in the separation of O_2/N_2.

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