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PERFORMANCE OF GRAPHENE OXIDE MEMBRANE DEPOSITED ON HOLLOW ALUMINUM FIBER IN H_2 SELECTIVITY WITH TEMPERATURE VARIATION

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Abstract

Introduction

The membrane separation process has gained prominence and has been used in a wide variety of applications, such as in gas separation processes. Ceramic supports with hollow fiber geometry have a larger area per membrane volume, which ensures greater productivity and better performance. Graphene oxide membranes deposited on different supports have been used successfully to separate various gases, including hydrogen (H_2) [1].
Considering this, in this work composite membranes of alumina hollow fiber coated with graphene oxide (GO) (α-Al_2O_3/γ- Al_2O_3/GO) were manufactured, aiming at relevant selectivity for H_2 in relation to CO_2 and N_2. The selectivity of the membrane was evaluated considering different temperatures (50, 100 and 150 °C) in order to establish a relationship.

Material and methods

The fibers used in the experiments were of the ceramic hollow fiber type (alumina), with asymmetric pore distribution. They were produced using the phase inversion method followed by sintering [2].
Before the GO deposition step on the fibers, a dip-coating process was carried out, immersing the fiber in boehmite at room temperature at a speed of 1 mm/s for 10 s. After the immersion step, the fibers were dried in an oven at 40 °C for 24 h and calcined in an oven at 650 °C for 3 h with a heating and cooling rate of 0.7 °C/min [3].
Graphene oxide was synthesized by the modified Hummers method [4].
The resulting suspension (1 mg/mL) was deposited on the fiber using the vacuum impregnation method [5].
To measure the flow of H_2, N_2 and CO_2 through the GO membranes, the membrane was first activated, which consists of allowing the passage of gas with a pressure of around 0.4 bar, with the purge closed for 1 h. After this period, gas flows are checked with a bubble meter at various pressures. The flow was measured at temperatures of 50, 100 and 150 °C. Measurements were carried out in triplicate and selectivity responses were analyzed using JMP Software (statistical analysis of data in relation to pressure and temperature).
The characterization of the membrane before and after coating was carried out according to its morphology and structure using a scanning electron microscope (SEM) (Carl Zeiss Model EVO MA 10).
The GO produced was structurally and morphologically characterized using the Raman spectroscopy technique.

Results and discussion

The conformity and adhesion of the GO layers to the fiber is represented in Fig. 1. It is possible to notice the formation of the layer with a thickness of 1.8 µm and high roughness, which can be explained by the solution deposition method. Furthermore, the presence of stacked GO flakes can be seen, forming a layer that creates a path for the passage of gases.

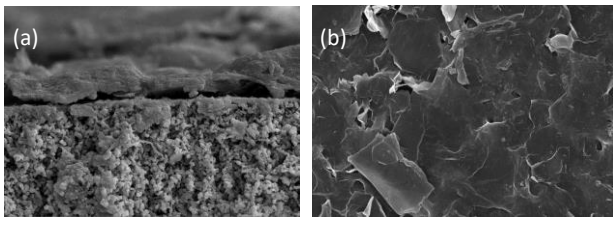

Fig. 1: MEV: (a) GO layer on the hollow fiber; (b) Structure of GO flakes.

Fig. 2 (a) presents the Raman spectra of the produced GO and pure graphite (GR) (starting material) for comparison purposes. All spectra exhibit characteristic peaks in the region between 1000 and 3000 cm^{-1} for argon laser excitation energy at 514 nm (2.41 eV).

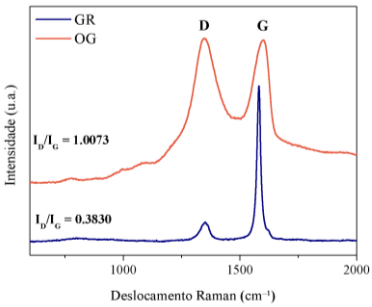

Fig. 2: Raman spectrum of GR and GO.

The ratio between the intensities of the D and G bands (I_D/I_G) quantitatively reveals the degree of disorder of the analyzed structure. As shown in the figure, for GR an I_D/I_G ratio = 0.3830 was observed and for GO, an I_D/I_G value = 1.0073. When $I_D/I_G > 1$ indicates interruption in sp^2 hybridization due to the large number of defects, while $I_D/I_G < 1$ is characteristic of a material with fewer structural defects and a better graphitic network [6].
Fig. 3 (a) shows the behavior of H_2/N_2 and H_2/CO_2 selectivity, considering the measurements of the fluxes of each gas through the GO composite membrane.

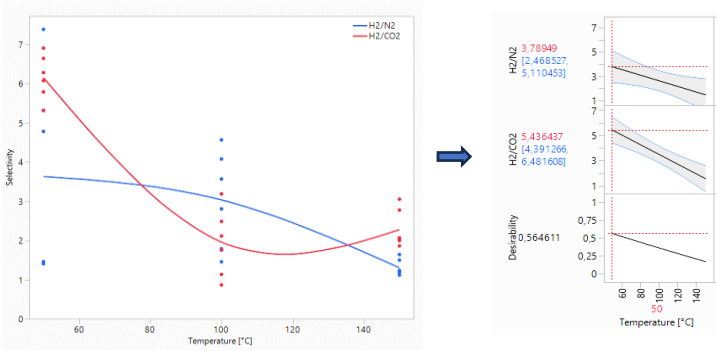

Fig. 3: H_2/N_2 and H_2/CO_2 selectivity curve and statistical data.

An overview of the statistical analysis shows that selectivity (relationship between flows) is optimized at the lowest temperature (50° C). This scenario occurs both for H_2 in relation to N_2, and for H_2 in relation to CO_2. Furthermore, statistical data revealed a relationship of selectivity decay with increasing temperature. This effect was explained by Yun et al. [8] which reports a decrease in permeability with temperature gradient. The proposed explanation is that at higher temperatures other gas passage mechanisms (such as diffusion) can be activated, thus altering the interaction between GO and gases. Another important factor is that heating the GO layer can cause shrinkage in its structure, increasing obstacles to the passage of gases. This result is of great relevance for a future industrial application, considering that the membrane can operate at low temperatures and provide selectivity to H_2, which reduces process costs and energy consumption.

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