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Influence of dip-coating times towards oxygen separation performance

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Abstract. Several advantages possessed by carbon membrane such as can be easily processed, high gas separation performance and requires adequate amount of energy compared to the conventional separation process are the reasons it is deemed as the future media of separation. This study utilized PI blends and nanocrystalline cellulose (NCC) to prepare the tubular carbon membrane in order to investigate its fabrication. The effect of dip-coating duration (15, 30, 45, and 60 min) on physicochemical properties O₂/N₂ separation was determined. Carbonization was done at 800 °C with 3 °C/min rate of heating under argon gas flow (200 mL/min). Tests of pure gas permeation were conducted in order to study the transport mechanism of prepared carbon membrane at ambient temperature and 8 bar of feed pressure. Carbon membrane with O₂ permeance of 29.92 ± 1.44 GPU and O₂/N₂ selectivity of 9.29 ± 2.54 were obtained after 45 min of dip coating.

Keywords: Dip-coating, Oxygen, P84 co-polyimide, Nanocrystalline cellulose (NCC), Tubular carbon membrane.

1. Introduction

Currently, gas separation is indicated among the main applications of membrane technology. Membrane application in gas separation attracts various attention from researchers around the globe mainly due to their benefits for example easy operation (no moving parts), requires low energy, as well as lesser footprint [1-4]. Various industrial applications demand for oxygen-enriched air such as medical, chemical and enhanced combustion processes. Cryogenic distillation [5] or pressure swing adsorption (PSA) [6] can be used to produce oxygen/nitrogen (O₂/N₂) contributing to 20 to 300 tonnes of oxygen per day with oxygen purity of more than 95%. However, this process is energy intensive [7, 8]. Previously, membrane technology utilization in separating O₂/N₂ or other gases are not extensively investigated. Membrane technology consumes low energy with moderate production volume compared



to the conventional gas production methods [9-11]. Various industrial or academic interests gained by the separation of O₂/N₂ via carbon membranes are attributed by their various benefits [12, 13]. The basis of O₂ separation are the pressure driven process. In the pressure driven process, the driving force is tempted by pressure variation between the upstream side and the downstream side. Membrane with nonporous structure is preferable in gas separation to avoid gas leaks across the membrane layer.

Until now, the large-scale production of commercial gas is in search for feasible membranes with high permeability and selectivity characteristics. Essentially, high permeability and selectivity as well as chemical and mechanical stability under long-term operation conditions are the characteristics that should be possessed by a membrane [14, 15]. Most review articles focus on discussing membrane development chronology in gas separation as well as the progress of various binary gases pair's separation. Compared to the previous reported articles, this work aims to investigate the current and updated progress of carbon membrane used in O₂ separation, via fabrication condition manipulation [16, 17]. Compared to polymeric membranes, carbon membrane's attractive features for example great thermal tolerance, chemical stability in eroding environment with beneficial gas permeability and selectivity balance are the main reason for its potential in gas separation [18, 19]. Preparation of carbon membranes was done via polymeric membrane carbonization at temperatures up to 900°C under controlled inert atmosphere [20, 21]. Meanwhile, the selected polymeric precursor membrane material need to be able to endure high temperature treatment without considerable amount of reduction while producing high yield of carbon. The carbon membranes properties of gas permeation and microstructure are dependent on polymer precursor types, methods of fabrication as well as the condition of carbonization [22].

This study applied the dip-coating method in fabricating the supported tubular carbon membrane. Currently, reported studies on coating condition effects on gas diffusion characteristics of tubular PI/NCC-based carbon membrane. The central attention of this work is to offer better understanding on dip-coating processes in controlling the tubular supported carbon membrane morphology. Coating time parameter is identified as the main influence to the dip-coating processes. Dip-coating techniques show high large scale production potential with the ability to substitute the spray coating and the conventional spin coating techniques due to no supported size limitation as well as low polymers utilization [23, 24]. Generally, techniques focused on obtaining tubular supported carbon membranes described in the literature are complicated with the need to increase the coating time in order to attain crack-free carbon membrane, which requires several cycles as well as exceptional care. Only few works on membranes advancement are defect-free through a single step dipping-drying-carbonization are reported [7, 11]. The focus of this study is on NCC incorporation as additive on the superior performance of carbon membrane via various dip-coating times of 15, 30, 45, and 60 min. Supported carbon membranes that are free of defects were prepared under argon environment (200 mL/min) at 800 °C carbonization end temperatures.

2. Experimental section

2.1. Materials

In this study, P84 co-polyimide also known as PI is chosen as polymer precursor obtained from Sigma Aldrich (Castel and Favre: 58698-66-1) [15]. Fabricated nanocrystalline cellulose (NCC) and newspaper which acts as an additive were obtained from the preceding study [23]. Desiccation of both polymers were done at 100 °C overnight with the purpose to eliminate any humidity before membrane preparation. N-Methyl-2-pyrrolidone (NMP) was used in this study as a solvent acquired from Merck (Germany). Meanwhile, the porous tubular support was bought from Shanghai Gongtao Ceramics Co., Ltd. Tubular support having 3 mm thickness and 8 cm length was utilized. The pore mean size of the tubular support is approximately 0.2 μm with 40–50 % porosity.

2.2. Preparation of tubular carbon membrane

NMP dissolves the PI using mechanical stirrer while removal of the trapped bubbles were done during the stirring process through sonication. At various coating periods, polymeric solution was used to dissolve the tubular support. Then, desiccation of the supported polymeric membrane was done for 24 h at 80 °C before being submerged for 2 h in methanol. Next, desiccation of the reinforced polymeric membrane was done for 24 h at room temperature before proceeding with heat treatment process. Two reiteration was conducted on the coating-carbonization process to ensure the defect-free carbon membrane was obtained. In order to prepare the membrane, carbonization process of the polymeric membranes was done through Carbolite horizontal tubular furnace in argon environment (200 mL/min) at 800 °C. Throughout the experiment, the heating rate was set constant at 3 °C/min. As the heating cycle completed, temperature of the membrane prepared was naturally reduced to ambient temperature. For the purpose of characterization, unsupported carbon membranes (flat sheet) were put in similar order.

2.3. Pure gas permeation measurements

The gas permeation system is employed in this study in order to evaluate the carbon tubular membranes as previously described in our earlier work [25]. Employment of 14 cm-long membrane tubular stainless-steel module was done with for the purpose of positioning the 8 cm carbon tubular membrane. In order to prevent leakages, the membranes were fixed with rubber O-ring as the membrane are inserted into the module. At transmembrane pressure of 8 bar, pure N₂ (3.64), and O₂ (3.46) gases were separately delivered into the module. Permeability (P/l) and selectivity (α) of the membranes were determined according to previous study [26].

3. Results and discussion

3.1. Gas permeation measurements

Table 1 presents the gas permeability performances of carbon membrane fabricated at various coating times. The result indicates the gas permeation performance with 45 min of coating times as the best among the other coating times due to better pinholes sealing and complete penetration through the membrane pores with sufficient coating time [29].

Table 1. Gas separation results for PI/NCC carbon membranes carbonized at a different coating times (n = 3, error analysis = $\pm 10\%$).

Sample	Carbon membrane		
	Permeance (GPU)		Selectivity
	N ₂	O ₂	O ₂ /N ₂
PI/NCC 15 minutes	3.08 \pm 3.65	22.67 \pm 1.84	7.36 \pm 2.11
PI/NCC 45 minutes	3.22 \pm 3.21	29.92 \pm 2.98	9.29 \pm 2.54
PI/NCC 30 minutes	3.18 \pm 4.16	25.53 \pm 3.51	8.03 \pm 2.43
PI/NCC 60 minutes	3.11 \pm 3.98	24.48 \pm 2.44	7.87 \pm 3.19

The order of gas permeance for the selected gases were O₂ > N₂. Variances in the performance of gas permeation were decided according to differences in carbon microstructure which directly influenced the transport mechanism of the membrane [19, 27]. According to the results, high selectivity at 45 min

is caused by pores reduction compared to those at 60, 30, and 15 min. Differences in pore features lead to predominance of various transport mechanisms on the membrane [18, 28]. Furthermore, sufficient time is available for the surface condition to be improved and the cracks of the highly porous support to be repaired.

4. Conclusion

Tubular carbon membrane was successfully produced via single-step dip-coating at 800 °C carbonization temperature under argon atmosphere with the introduction of PI/NCC membrane. The aspect of dip-coating time in the coating technique was investigated in this research. Results produced indicate 45 min of carbon membrane dip-coated time as the best coating time. It is impossible for formation defect on the supporting material to be covered by polymeric solution at shorter dip-coating time. Nevertheless, longer dip-coating time leads to thicker membrane layer thus reducing the carbon membrane. According to the result, the highest O₂/N₂ selectivity of 9.29 ± 2.54 were achieved with O₂ permeance of 29.92 ± 2.98 GPU.

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