Carbon membranes for oxygen enriched air – Part I: Synthesis, performance and preventive regeneration

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ABSTRACT

Chemisorption of oxygen on the active sites of carbon layers limits the use of carbon membranes in air separation application. A novel online electrical regeneration method was applied to prevent the active sites on carbon surface to be reacting with O_2 while the membrane was in operation. This method reduced the aging effect and the membrane showed relative stable performance with only 20% loss in O_2 permeability and 28% increase in O_2/N_2 selectivity, over the period of 135 days using various feeds containing H_2S, *n*-Hexane and CO_2-CH_4 gas. The carbon membranes reported here were produced at the pilot-scale facility by the carbonization of regenerated cellulose under optimized conditions to achieve good air separation properties. The permeation properties of the membranes were tested by single gas separation experiments at 5 bar feed pressure (50 mbar permeate) and temperature range 20–68 °C. It was observed that O_2 permeability is increasing exponentially with increase in operating temperature without significant loss in the O_2/N_2 selectivity. The O_2 permeability of 10 Barrer *(1 Barrer = 2.736E − 09 m^3(STP)m/m^2 bar h)* with O_2/N_2 selectivity of 19 was achieved at 68 °C. Thermal (80 °C), chemical (propylene) and online-electrical (10 V DC) regeneration approaches were studied to lessen the aging effect on carbon membranes.

1. Introduction

At present, the air separation market to produce pure oxygen (O_2: 95–99.99%) is dominated by cryogenic fractionation and pressure swing adsorption because current membranes are not capable of economically producing membranes with comparable purity [1]. The separation is based on the difference in permeation rates of oxygen and nitrogen through the membrane, and the performance of polymeric membranes is restricted by the trade-off between permeability and selectivity [2]. Polymeric materials may have a high permeability for O_2, but rather low O_2/N_2 selectivity (usual range 2–8), and the maximum permeate purity achievable for O_2 with these membranes seems to be 30–60% [3].

Carbon is one class of material that can offer improved performance due to molecular sieving effect. In molecular sieving, the available pore size is below the kinetic diameter of one of the gas components in the feed. This characteristic of the material increases selectivity by reducing the rotational degrees of freedom of nitrogen versus oxygen in the diffusion (kinetic) transition state. Carbon membranes (CM) can be prepared by carbonization of the precursor membranes at high temperature (550–850 °C) under vacuum or in an inert environment (Ar, He or N_2). Gas permeation properties of CM are affected by the type of

precursor and carbonization conditions. Many authors have reported high selectivity and permeability of carbon membranes (CM) compared to polymeric membranes for air separation [4–7].

Although CM have reported better performance compared to polymeric membranes, the operational stability and aging are the important issues to be considered for the implementation of these carbon membranes. CM usually age very rapidly due to physical aging (pore shrinkage to achieve a thermodynamically stable structure and or physical adsorption of gas molecules) and or chemical aging (chemical bonding, usually C=O bonds) [8–11]. This aging effect may seriously reduce the permeability of a membrane and hence it is still a major problem for the industrial application of CM in air separation where the membrane is exposed to O_2 all the time.

Several techniques have been reported to achieve a stable performance of CM under oxygen environment. Menendez et al. [11] used *thermal regeneration* and found that thermal treatment of membranes at 120 °C in a vacuum could remove oxygen-containing surface groups from activated carbons. However, the regenerative effect is very brief because it leaves a surface with reactive carbon sites that can re-adsorb oxygen very quickly even at room temperature. *Chemical regeneration* requires an addition of a chemical (gas) to restore the membrane performance. Jones and Koros [12] tested purging of propylene at about

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10 bar to restore the membrane performance, however, the permeance of O_2 was not successfully recovered.

Lie et al. [13] studied *electrothermal regeneration* to enhance the permeation of CO_2 in iron-doped flat-sheet CM. They applied a direct current of 30 mA (17.5 V) on the iron-doped CM and studied the effect of pulsating electrothermal regeneration (i.e. electric current set to "on" and "off" periodically). After electrothermal regeneration, the CO_2 permeability was 65% higher compared to initial value because the sorption of gases in carbon matrix was reduced, while diffusivity was increased to a considerable extent. Nevertheless, the membrane without any regeneration showed 60% loss in permeance of CO_2.

The aim of the current study has been to exploit further the electrically conductive nature of CM to enhance or stabilize the performance of the membrane. The present paper focuses on the novel online-regeneration method to prevent the reactive/adsorption sites by supplying continuous electric current. The effect of "online electrical regeneration (regeneration parallel with separation process)" on carbon hollow fiber membranes has not been fully explored, and there is not much information available on this topic. Hence, an online regeneration (DC: 44–55 μA, 10 V) was tested in this study to achieve a stable performance of CM in air separation application. In addition, thermal and chemical regeneration methods were also pursued to find an effective, simple, and economical solution to restore the membrane performance. The term "Preventive electrical regeneration" (PER) is used for the electric regeneration in this study. PER means a continuous supply of electrical potential during membrane operation to prohibit the molecules adsorbing on the membrane surface.

2. Theory and background

2.1. Structure of carbon molecular sieve

Carbon molecular sieve (CMS) is derived from organic thermosetting precursors by heat treatment in vacuum or in an inert environment. Geiszler and Koros [14] reported that an inert gas (Ar, He or N_2) atmosphere resulted in more open, but less selective CMS matrix compared to vacuum carbonization. They explained this with acceleration in the carbonization process due to increased gas phase heat and mass transfer. By increasing the final temperature in polyimide carbonization from 550 °C to 800 °C (in vacuum of He gas), the authors observed a decrease in permeance while selectivity increased. Precursors for CMS include thermosetting resins, graphite, coal, pitch, plants and synthetic polymers [15].

Bisco and Warren [16] introduced the concept of turbostratic order for graphitic carbons. The carbon consists of turbostratic groups, where each group has several graphite layers stacked together roughly parallel and equidistant, but with each group having a random orientation as shown in Fig. 1(a). Packing imperfection between the stacked layers contains slit-like pores which give rise to the molecular sieving

structure and have a bimodal pore size distribution. The edges of adjacent stacked layers are believed to make the slit-like ultra-micropores (≤ 0.7 nm), while micropores (0.7–2 nm) are formed between the planes due to the random orientation of the adjacent carbon sheets [6]. The gases may diffuse through the pores, or they may adsorb on the walls and travel through the pores by a mechanism known as surface flow [17]. The bigger, more strongly adsorbed molecules may also block the pores of smaller molecules in a phenomenon known as competitive adsorption or selective surface flow. This results in reverse selectivity; the smaller components are thus retained.

2.2. Electrical regeneration

The continuous medium of graphene sheets makes the CMS membranes electrically conductive. As shown in Fig. 1(b), each sp^2-hybridized carbon atom combines with three other sp^2-hybridized atoms to form a series of hexagonal structures, all located in parallel planes. The fourth valency, that is, the free delocalized electron, is oriented perpendicular to this plane as shown in Fig. 1(b). Unlike the sigma (σ) orbital, it is non-symmetrical and is called by convention a pi (π) orbital [18].

An adsorbed gas, such as CO_2, may be quickly and efficiently desorbed by the passage of a direct current (DC), thereby allowing for a low-energy, electric swing separation system with operational simplicity [19]. The van der Waals forces between the carbon skeleton and the adsorbent are disrupted or perhaps reversed by the electric current. This interaction most likely results from the quadrupole moment and the free electrons of CO_2. As a result, adsorbed CO_2 is released or repulsed from the micropore surface and desorption occurs. The same effect may apply to other adsorbed gases.

Electrothermal desorption is a process where the heat is generated inside the adsorbent. Hence, the heat and mass flux directions are the same, i.e. from solid to the fluid, as opposed to traditional thermal regeneration. Petkovska and Mitrovic [20] reported that electrothermal desorption is more energy efficient than conventional desorption because the fluid temperature can be substantially lower than the adsorbent temperature determining the adsorption equilibrium. They also showed that same direction of heat and mass fluxes results in better desorption kinetics. The ohmic heating enhancing desorption, probably discourage adsorption at the pore entrances. For this reason, optimization of current cycle time, to stabilize or increase the permeability of relevant gas is believed to be important.

The electrical resistance R (Ω) can be evaluated from media resistivity and its dimensions [21] as shown in Eq. (1).

$$R = \frac{\rho L}{e \ell} \tag{1}$$

where ρ is electrical resistivity of the material (Ωm), L is the length of material (m), e is the width (m) and ℓ is the thickness (m). Resistivity is
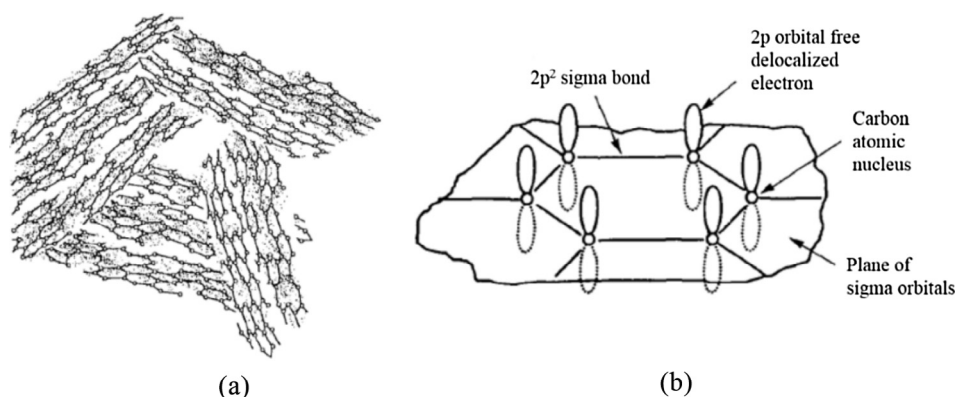

Fig. 1. (a) Structure of turbostratic graphite and (b) Schematic of sp^2 hyberdized structure of graphite sheet showing 2p free electrons [18].