



Effect of pyrolysis temperature and operating temperature on the performance of nanoporous carbon membranes

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ABSTRACT

Technology designed to capture and store carbon dioxide (CO₂) will play a significant role in the near-term reduction of CO₂ emissions and is considered necessary to slow global warming. Nanoporous carbon (NPC) membranes show promise as a new generation of gas separation membranes suitable for CO₂ capture.

We have made supported NPC membranes from polyfurfuryl alcohol (PFA) at various pyrolysis temperatures. Positron annihilation lifetime spectrometry (PALS) and wide angle X-ray diffraction (WAXD) results indicate that the pore size decreases whilst the porosity increases with increasing pyrolysis temperature. The membrane performance results support these findings with a significant increase in permeance being seen with increasing pyrolysis temperature, which relates to the increase in porosity.

Mixed gas performance measurements also show an increase in CH₄ permeance as the operating temperature is increased from 35 to 200 °C, which can be related to an increase in the rate of diffusion. However, the selectivity decreases with increasing operating temperature due to the smaller changes in the CO₂ permeance. These smaller changes in CO₂ permeance can be related to the stronger adsorption of this gas on the carbon surface at lower operating temperatures. Interestingly, regardless of the original pyrolysis temperature, the selectivity at higher operating temperatures is similar, whereas the permeance remains related to this pyrolysis temperature.

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1. Introduction

1.1. CO₂ sequestration and nanoporous carbon membranes

Capture and geological storage (sequestration) of carbon dioxide (CO₂) from emission sources has great potential as a socially acceptable solution to significantly reduce greenhouse gas emissions in the interim until sustainable energy solutions are developed and implemented. A significant challenge for the successful implementation of the CO₂ sequestration process is reducing the capture cost. The development of new efficient materials for CO₂ separation, such as nanoporous carbon, have great potential for reducing the capture cost.

There are several points within stationary energy production where CO₂ is produced and then emitted to the atmosphere. The first is in the production of natural gas (primarily methane CH₄) from an underground reservoir. In this case, the CO₂ coexists with methane in the reservoir. The CO₂ must be removed from the natural gas before it can be used in a commercial or domestic application. In Australia, this is currently done via onshore gas processing plants but it can also be completed on offshore processing platforms, in which case the development of technologies with a small weight and footprint, such as membranes, is very important. The second emission source comes from the production of synthesis gas (primarily hydrogen) using fossil fuels such as natural gas, oil and coal. Another emission source is the flue gas from electricity power stations that are from direct combustion of fossil fuels, such as natural gas, oil or coal.

Nanoporous carbon (NPC) membranes show promise for separating CO₂ from natural gas and synthesis gas production. Unlike their polymeric counterparts, NPC membranes are not adversely

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affected by higher operating temperatures, which make them ideal for natural gas and synthesis gas separation.

However, NPC membranes are adversely affected by the combined presence of oxygen and water [1–3]. Given the presence of both oxygen and water in power station flue gases, NPC membranes would not be suitable for capturing CO₂ from this stationary emission source. Additionally, as power station flue gases are at atmospheric pressure, there is little driving force available for membrane separation unless the permeate stream is operated under vacuum.

1.2. Material manufacture

Nanoporous carbon is produced from the pyrolysis (heating) of a polymer in an inert atmosphere. As the temperature is increased, the polymer degrades leaving a porous carbon structure with nanosized pores that are suitable for gas separation. Supported nanoporous carbon (NPC) membranes are made by coating the polymer onto a porous support prior to pyrolysis.

NPC membranes have been a subject of interest for several decades and have been made from a variety of polymers. High performance NPC membranes have been manufactured from cellulose [4–9], polyvinylidene chloride (PVDC) [10], phenolic resin [11], polyimide [12,13], polyamic acid [14] and polyfurfuryl alcohol (PFA) [15]. The CO₂/CH₄ separation factors of these NPC membranes reported by the aforementioned researchers range from 10 to as high as 200. The current paper focuses on PFA as a precursor as this polymer produces a high yield of nanoporous carbon with good selectivity [16].

The final pyrolysis temperature has a significant impact on the resulting performance of the NPC membrane. The evolution of the nanoporous carbon structure with increasing pyrolysis temperature has been studied for carbon molecular sieves (CMS) derived from PFA [17–19]. Foley et al. [18] explain that as the pyrolysis temperature is increased from 300 °C, the PFA precursor begins to produce a carbon solid. At temperatures above 500 °C, the hydroxyl groups disappear and when the pyrolysis temperature is increased beyond 600 °C, dehydrogenation occurs and finally at temperatures above 1200 °C where all of the hydrogen has been removed, a rearrangement of the carbon atoms occurs that ultimately produces a graphite-like structure.

Nuclear magnetic resonance (NMR) spectra of CMS samples prepared at 400, 500 and 600 °C by Mariwala and Foley [19] have showed the presence of oxygen atoms, as are present in the original PFA polymer, at pyrolysis temperatures up to 500 °C whilst at 600 °C elemental analysis reveals the presence of only carbon with less than 0.5% hydrogen. Powder X-ray diffraction on samples prepared at higher pyrolysis temperatures have revealed a shift in the *d*-spacing from between 3.9 and 5.2 Å at 500 °C to between 3.7 and 3.9 Å at 800 °C and then 3.6 Å at 1000 °C.

The narrowing of the pore size distribution with increasing pyrolysis temperature is said to be caused by the growth of the aromatic microdomains that also cause a subsequent increase in porosity. However, the removal of oxygen and carbon–hydrogen bonds with increasing pyrolysis temperature leads to a fragile structure and the collapse of the micropores [19].

In a more recent study of bulk nanoporous carbon, Burket et al. [20] used a variety of characterisation techniques to further understand the carbonisation of PFA in the range from 300 °C up to 600 °C. It was concluded that between 300 and 400 °C, carbon and polymer carbon chains co-exist resulting in a mesoporous structure. As the temperature is increased beyond 400 to 600 °C, with the major weight loss at 500 °C, carbonisation completes and the mesopores collapse leaving a microporous structure.

Looking specifically at membranes, Shiflett and Foley [16] have produced three NPC membranes from PFA at pyrolysis temperatures of 300, 450 and 600 °C using ultrasonic deposition. Increasing the pyrolysis temperature from 300 to 600 °C increased the oxygen (O₂) and nitrogen (N₂) permeance by an order of magnitude, which the authors attribute to the increase in porosity.

Interestingly, the majority of NPC membranes that have been manufactured from PFA are at pyrolysis temperatures at and below 600 °C [16,21–24]. Whilst a complete nanoporous carbon structure is produced at a pyrolysis temperature of 600 °C with a continuous reduction in pore size and increase in porosity achieved at temperatures greater than 600 °C, the apparent fragility of the structure beyond 600 °C makes it difficult to work with in a membrane form.

1.3. High temperature operation

Given the high temperatures at which NPC membranes are manufactured, they are ideal for operation at high temperature. High temperature operation is advantageous for CO₂ separation from natural gas or synthesis gas production as it eliminates the need for pre-cooling, which is required when using polymeric membranes. Therefore, understanding how high temperature operation affects the transport mechanism and the performance of NPC membranes is pertinent.

The transport of gases through NPC membranes at ambient temperatures is considered to be a combination of surface diffusion and molecular sieving [4,11,25–31]. When the pore size of the membrane is less than 10 Å but greater than 5 Å, the more polar gas molecules are selectively adsorbed onto the surface of the membrane and move through via surface diffusion [25]. Surface diffusion is the mechanism proposed by Rao and Sircar [25] for gas flow through the surface selective flow (SSF) membranes manufactured from the pyrolysis of polyvinylidene chloride.

Gas separation via molecular sieving will occur when the pore sizes of the membrane approach the size of gas molecules (<5 Å) as is generally the case for NPC membranes manufactured from the pyrolysis of PFA. Gas molecules smaller than the membrane pores will pass through whilst larger molecules will be retained on the high-pressure side of the membrane. However, if there are some defects or minor cracks present in the membrane, there will be pore sizes larger than 5 Å and surface diffusion may also contribute to the overall performance.

The research work of Fuertes [26] provides a good explanation of the transition between molecular sieving and surface diffusion. Fuertes oxidised the NPC membranes produced from the pyrolysis of phenolic resin to increase the pore size of the nanoporous carbon from 4 Å to 5–7 Å. It was noted that in the non-oxidised membranes the permeance of a gas increases with decreasing molecular size, which suggests a molecular sieving mechanism. However, in the oxidised membranes with the larger pore size, permeance was no longer correlated with molecular size as the larger more condensable molecules such as hydrocarbons displayed increased permeance.

Both surface diffusion and molecular sieving are activated mechanisms that follow an Arrhenius-type relationship dependent on the operating temperature (*T*) [27]. To simplify the situation when the relative contribution of surface diffusion and molecular sieving is unknown, Suda and Haraya [27] developed a generalised relationship for the permeance (*P*) (Eq. (1), where *E_p* is the activation energy of permeation) to include the apparent activation energy for diffusion (*E_d*) and heat of adsorption (ΔH_{ads}) (Eq. (2)).

$$P' = P'_0 \exp \left[\frac{-(E_p)}{RT} \right] \quad (1)$$

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