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# Separation of $NF_3$ and $CF_4$ using amorphous glassy perfluoropolymer Teflon AF and Hyflon AD60 membranes

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## ABSTRACT

In this study, the pure and mixed gas permeabilities of Teflon AF2400, Teflon AF1600 and Hyflon AD60 membranes towards $NF_3$ and $CF_4$ were measured to determine whether membrane gas separation can be applied to purify $NF_3$ of $CF_4$. In accordance with literature results, it was shown that thermal annealing of the solution cast films was necessary to reach optimum performance, wherein all membranes studied had a preferential permeation of $NF_3$ rather than $CF_4$. The Teflon AF and Hyflon AD60 membranes displayed rather high pure and mixed gas selectivities ($\alpha(NF_3/CF_4)$) considering the high free volume of the polymers. Furthermore, the $\alpha(NF_3/CF_4)$ increased with increasing diffusion selectivity of the glassy perfluoropolymers, of which the pure gas He/$N_2$ ideal selectivities gave an indication, and which is related to the fractional free volume (FFV). As a result, Hyflon AD60 displayed the highest $NF_3/CF_4$ pure and mixed gas selectivity of just above 12, albeit with a rather low $NF_3$ permeability of ca. 1.9 Barrer. Although the membranes were sufficiently inert towards penetrant induced swelling, a Hyflon AD60 membrane swollen by residual casting solvent displayed an increase in the pure and mixed gas $NF_3$ and $CF_4$ permeabilites and reduced selectivity compared to that of an annealed, fully relaxed Hyflon AD60 membrane.

## 1. Introduction

Nitrogen trifluoride ($NF_3$), serves as a convenient fluorine source that is used mainly in the electronic and semiconductor manufacturing industry for plasma assisted etching of silicon wafers and cleaning of chemical vapour deposition chambers [1–4]. The use of $NF_3$ as etchant rather than perfluorocarbon gases (PFCs) such as carbon tetrafluoride ($CF_4$) and perfluoroethane ($C_2F_6$) is motivated by the fact that $NF_3$ displays superior etching performance and does not lead to the build-up of carbonaceous residues [4,5]. Fearing defect formation during high density integrated circuit manufacture as a result of potential carbonaceous build-up, the electronic manufacturing industry demands high purity $NF_3$ (VLSI-grade $NF_3$) in which the $CF_4$ content must be below 20 ppm [6]. This is a challenging specification to reach, as $NF_3$ is usually contaminated with the physically and chemically similar $CF_4$ when obtained from the so-called two-step synthesis procedures [7,8] that uses electrochemically produced fluorine ($F_2$) as a reactant. $CF_4$ contamination originates during the electrochemical production of $F_2$ from the decomposition of carbon anodes in the fluorine-rich environment [3], whereas alternative $NF_3$ electrochemical synthesis methods, in which nickel anodes are used, are often not used due to various other disadvantages [3,9].

Purification of $NF_3$ from $CF_4$ is therefore crucial to meet the high standards set by the electronic industry, but this has proven to be a daunting task. Although adsorption processes using porous zeolite adsorbents have been the most popular approach [10–12], distillation processes have also been developed [13,14] for the separation of $CF_4$ from $NF_3$. Cryogenic distillation of $NF_3$ and $CF_4$ would be impractical due to the small difference of 1 °C in the normal boiling points of $NF_3$ and $CF_4$ [15]. As a result, extractive distillation processes have been developed wherein entraining agents such as hydrochloric acid [13] and ionic liquids [14] have been used to enhance the efficiency of separation. A major drawback with zeolite adsorbents is that $NF_3$, the major component, is preferentially adsorbed [10–12], thus requiring high adsorbent volumes that need to be periodically regenerated. In this regard, a polyacrylonitrile-based carbon molecular sieve, Carbosphere®, has been claimed to preferentially adsorb the minor component, $CF_4$ [6], which represents a more efficient separation approach.

Gas separation using polymeric membranes has enjoyed major developments since they were first used on industrial scale in the 1980s for hydrogen separation [16,17]. Industrially, membrane based separations offer the advantage of being more energy

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efficient when compared to conventional gas separation methods such as adsorption and cryogenic distillation. In addition, advances in polymer chemistry have led to the development of membrane materials that offer a better trade-off between permeability and selectivity [18–20]. This trade-off remains a major obstacle preventing the widespread implementation of this technology. However, membrane gas separation has been used for the recovery of PFCs, such as perfluoroethane ($C_2F_6$), from semiconductor manufacturing plants in which the unreacted gases are separated from diluents such as $N_2$ using glassy polymers [21–23]. These membrane recovery methods [21–23] have also been mentioned to be suitable for the recovery of $NF_3$ and $CF_4$, however, to the best of our knowledge, no membrane based separation method for the purification of $NF_3$ from $CF_4$ has been published.

In this study, the polymer membrane based separation of $NF_3$ and $CF_4$ was therefore investigated to establish the applicability of the technology to this rather difficult separation challenge. High performance glassy perfluoropolymers of Teflon AF and Hyflon AD60, which display permeability–selectivity relationships that lie close to the current Robeson upper bound [18], were used. Considering the oxidising character of $NF_3$ [1], these polymers also offer satisfactory stability due to their fluorinated structure. It is further known that PFCs such as $CF_4$ are significantly more soluble in perfluorocarbon polymers compared to conventional hydrocarbon based polymers [24,25], which would therefore also lead to increased permeabilities. Consequently, pure and mixed gas permeability and selectivity was determined, wherein the GC method described in our previous work [26] was used for quantitative analysis during the mixed gas permeability experiments. It is shown that surprisingly good permeability selectivity towards $NF_3$ was obtained, which showed a clear dependence on the FFV of the polymer membranes.

## 2. Experimental

### 2.1. Materials

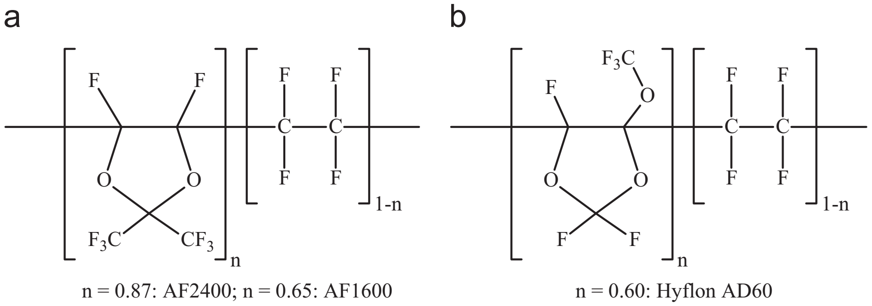
The random copolymers of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD) containing 87 and 65 mol% BDD (Fig. 1(a)), which is commercially available as Teflon AF2400 and Teflon AF1600 respectively (Du Pont, Wilmington, DE) were used as received. For the sake of brevity, Teflon AF2400 and Teflon AF1600 will be referred to in the text as AF2400 and AF1600 respectively. The random co-polymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluorometoxy-1,3-dioxole (TTD) containing 60 mol% TTD (Fig. 1(b)), commercially available as Hyflon AD60 (Solvay Solexis, Italy) was used as received. Additionally, Fluorinert™ FC-770, a perfluoro N-alkylmorpholine with a normal boiling point of 95 °C (3 M, Belgium), and PTFE films (manufactured by PALL Corporation, USA) were used as received.

Nitrogen trifluoride ($NF_3$), certified to be 99.99 vol% pure was purchased from Linde Electronics South Africa (Pty) Ltd. (LESA Grade) and tetrafluoromethane ($CF_4$) with a certified purity of 99.99 vol%, purchased from Air Liquide, Germany GmbH, were used for pure and mixed gas membrane permeability and selectivity measurements. Nitrogen ($N_2$) and helium (He) both with a purity of 99.999 vol%, were purchased from Air Products, South Africa, and were used for pure gas membrane permeability measurements. He of the same purity was also used as the carrier gas in the on-line gas chromatographic (GC) system that was used for sample analysis.

### 2.2. Membrane preparation

Isotropic, dense films of all three of the amorphous, glassy fluoropolymers (Fig. 1) were prepared by the solution casting method with Fluorinert™ FC-770 as solvent and polymer solutions with concentrations of 2 wt% for AF2400 and 4 wt% for both AF1600 and Hyflon AD60. Each solution was agitated continuously at room temperature with a magnetic stirrer for at least 16 h so as to obtain homogenous solutions. Glass templates consisting of flat, smooth glass discs and flanged glass cylinders that fitted together to form small containers were used for the polymer film preparation. These templates were filled with 5 mL of the AF2400 solutions and 2–2.5 mL of the AF1600 or Hyflon AD60 solutions, and the solvent was allowed to evaporate at room temperature for at least two days (48 h), while the cylindrical sections of the templates (approximately 4 cm in depth) were covered with watch glasses in the case of AF2400, and overturned funnels in the case of AF1600 and Hyflon AD60 to slow the rate of evaporation.

After solvent evaporation, the films were removed from the templates by the addition of deionised water before being dried on a paper towel. The clear, transparent circular films were then heat treated in two separate stages to ensure complete solvent removal. First the films were heated in a convection oven, without controlling the heating rate, to 125 °C for AF2400, 65 °C for AF1600 and 50 °C for Hyflon AD60, and were kept at the respective temperatures for at least 16 h. These temperatures were chosen so as to avoid deformation of the films during heating and are approximately 100 °C below the respective glass transition temperatures of each polymer. The films were cooled to room temperature without controlling the cooling rate and stored. During the second heat treatment, the films were annealed by heating in a GC oven from 30 to 200 °C for AF2400 and AF1600, and to 170 °C for Hyflon AD60 at a rate of 0.2 °C/min, kept constant at the maximum temperature for 30 min followed by cooling at a rate of 0.4 °C/min to 30 °C after which the temperature was kept constant for at least 30 min to ensure that thermal equilibrium had been reached. For the annealing stage, the membranes were placed on porous, hydrophobic PTFE films that were stretched over petri dishes onto which the films adhered after the annealing cycle. The AF2400 and AF1600 films could be easily removed from the PTFE support films, whereas the Hyflon AD60 membranes were used in the resulting composite form.



n = 0.87: AF2400; n = 0.65: AF1600

n = 0.60: Hyflon AD60

**Fig. 1.** Molecular structure of (a) Teflon AF and (b) Hyflon AD60 amorphous, glassy perfluoropolymers.