

## Development of perfluorocarbon-based supported liquid membranes for gas separation

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## 論文の内容の要旨

論文題目: Development of perfluorocarbon-based supported liquid membranes for gas separation

(気体分離のためのパーフルオロカーボン液体膜の開発)

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The focus of this thesis is the investigation of supported liquid membranes based on perfluorocarbons (PFCs) as the active barriers for the separation of different gas species. Perfluorocarbons are liquids chosen for their chemical inertness and ability to dissolve large amounts of gases. These liquids have not been applied in membranes before, but their physical features make them good candidates. The membranes were developed to separate mainly H<sub>2</sub> and O<sub>2</sub> at close to room temperatures and atmospheric pressure for their application in photocatalytic water splitting, but other separations such as H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> were also studied. The perfluorocarbons utilized in this study were perfluorotributylamine (PFTBA) and perfluorooctanol (PFO) selected because of their relatively low vapor pressures and high chemical stability.

The PFCs were imbued on inorganic supports made of porous alumina tubes of pore size of 5 and 60 nm. The characterization of the supports consisted of estimation of their tortuosity and porosity. The porosity was measured by two different methods, a water saturation technique and a grayscale analysis of the support. The water saturation technique consisted of saturating the void spaces in the support with water and measuring the water uptake. A porosity ranging between 0.32 - 0.36 was obtained. The grayscale analysis consisted of determining the area covered by pores and particles in an SEM image by analyzing the dark and light regions in the images. The grayscale method revealed a porosity ranging between 0.3 - 0.4 in good agreement with the water saturation method. Finally, the support was subject to single gas permeation tests for H<sub>2</sub> and O<sub>2</sub> to determine the diffusive mechanism across the pores. The support had an H<sub>2</sub>/O<sub>2</sub> selectivity of 4.5 in close agreement to the value of 4.0 expected for Knudsen diffusion. From this the tortuosity was determined to be 1.24.

To prepare the supported liquid membranes, the perfluorocarbons, PFTBA and PFO were imbued into the dry porous alumina supports. They were subject to tests at different operating conditions in order to determine their permeation properties. The results with PFTBA will be reported first. The membrane displayed a H<sub>2</sub>/O<sub>2</sub> selectivity of 40 with a H<sub>2</sub> single gas permeance of  $3.0 \times 10^{-10} \text{ mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$  at a temperature of 40 °C and a flow rate of 50

$\text{cm}^3 \text{min}^{-1}$ . Equimolar mixtures of  $\text{H}_2/\text{O}_2$ ,  $\text{O}_2/\text{N}_2$  and  $\text{H}_2/\text{N}_2$  were tested, achieving selectivities of 140, 60 and 100 with  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  permeances of  $1.0 \times 10^{-9}$ ,  $8.0 \times 10^{-10}$  and of  $1.0 \times 10^{-9} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ , respectively at temperature of  $40^\circ \text{C}$ . Higher flow rates and higher temperatures showed no significant impact on the separation performance of the membrane, but decreased the lifetime of the membrane. This was the result of higher liquid loss by evaporation.

Results with the PFO membrane were similar. The membrane displayed a  $\text{H}_2/\text{O}_2$  selectivity of 50 with a  $\text{H}_2$  single gas permeance of  $2.0 \times 10^{-10} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$  at the same conditions of the PFTBA membrane. The stability of the PFO membrane was higher than the PFTBA membrane and this was attributed to the lower vapor pressure of PFO.

Stability under water vapor is important for separating streams from photocatalytic water splitting. A study on water resistance was performed by separating the 50/50 mix gas at different humidity conditions with both membranes. The test revealed that the performance of the membranes was not affected, but their lifetime was reduced at high levels of humidity. This phenomenon could be the result of water interacting with the alumina support.

Improved stability towards evaporation is important and the effect of the pore size of the membrane was also investigated. The standard 60 nm pore-sized support was substituted by a 5 nm pore-size material and it was verified that the latter increased stability. This is because the smaller pores promote capillary condensation by reducing the vapor pressure of the liquid inside the pores reducing the vaporization of the liquid. This consequently prolonged the lifetime of the membrane, especially when the membrane was operated at higher temperatures. A partial pressure analysis was performed by diluting the 50/50 mixed gas partial pressure with argon gas. The experiment showed that in the PFTBA membrane,  $\text{O}_2$  is limited by solubility and that a decrease in pressure leads to higher  $\text{H}_2$  competition for solubility sites which resulted in higher selectivities. The PFO membrane was not influenced by the change in partial pressure since the permeance of both gases changed proportionally.

The solubility and diffusivity of  $\text{H}_2$  and  $\text{O}_2$  were estimated by means of a time-lag method for both PFTBA and PFO. This method consisted in determining the transient permeance behavior of the gas species. The PFTBA membrane presented  $\text{H}_2$  and  $\text{O}_2$  solubilities of  $5.4 \times 10^{-4}$  and  $2.1 \times 10^{-4} \text{ mol m}^{-3} \text{Pa}^{-1}$  with diffusivities of  $1.8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$  and  $3.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively. The solubility of  $\text{H}_2$  and  $\text{O}_2$  in PFO were  $4.1 \times 10^{-4}$  and  $5.4 \times 10^{-4} \text{ mol m}^{-3} \text{Pa}^{-1}$  with diffusivities of  $1.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$  and  $3.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively. The solubility of  $\text{O}_2$  on the PFCs is of the same magnitude as  $\text{H}_2$ . However, the diffusivity of  $\text{H}_2$  surpasses  $\text{O}_2$  in both PFO and PFTBA.

The PFC-based membranes behaved as a sieving net allowing the permeance of the gases in the order of  $H_2 > O_2 > N_2$  according to the molecular size of the gas. These membranes presented a record performance when compared to conventional ionic liquid membranes. For instance, the ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF<sub>4</sub>], showed a maximum  $O_2/N_2$  selectivity of 6 with an  $O_2$  permeance of  $3.4 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . In addition, this ionic liquid was found to have poor wettability in the alumina supports displaying liquid droplets with contact angles of 35 to 42°. Conversely the PFCs showed perfect wettability.

A process flow simulation was performed to determine the feasibility of application of these membranes. The simulation was developed in Aspen Plus and targeted a hydrogen production of 1000 Kg day<sup>-1</sup>. The simulation revealed that a  $H_2$  recovery of 90% is possible with a purity of 99% which is competitive with conventional gas separation methods such as pressure swing adsorption (PSA). In addition, the process flow included a procedure to recover the PFC evaporated from the membrane.

To summarize, novel membranes with good permeation were developed. The membranes are able to separate hydrogen and oxygen at close to room temperature and atmospheric pressure. The mechanism of permeation was by solution/diffusion and the diffusivities depended on the size of the permeating species. Process simulations indicated that the membrane technology is competitive with conventional pressure swing adsorption.