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Supported fluorocarbon liquid membranes for hydrogen/oxygen separation

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ABSTRACT

Photocatalytic water splitting is an environmentally-friendly method for hydrogen formation, but usually H_2 and O_2, are produced together, so separation is needed. This paper describes the separation of the gases with supported liquid membranes. The permselective liquids were various perfluorocarbon-based fluids, Dimethyl perfluorosebacate ($(CF_2)_6(COOCH_3)_2$), ethyl perfluorononanoate ($CF_3(CF_2)_7COOC_2H_5$), perfluoro(perhydrophenanthrene) ($C_{14}F_{24}$) and 1H,1H,2H,2H-perfluorodecyl acrylate ($CF_3(CF_2)_7(CH_2)_2OCOCH{=}CH_2$). It was found that the perfluorodecyl acrylate-based liquid membrane showed the highest performance with H_2 permeance of 2.4×10^{-9} mol m^{-2} s^{-1} Pa^{-1} (6700 barrers) and a H_2/O_2 selectivity of 10. The permeance properties of H_2 and O_2 were measured by a time-lag technique and respective diffusivities of 1.1×10^{-8} and 6.7×10^{-9} m^2 s^{-1} and solubilities of 2.7×10^{-4} and 4.1×10^{-5} mol m^{-3} Pa^{-1}, were obtained. The lifetime of the membrane was over 48 h, which was much longer than that of other perfluorocarbon-based liquid membranes. The membrane was also stable at humid conditions.

1. Introduction

Hydrogen is an important substance that is used in diverse applications such as a reactant in hydrogenation reactions and a fuel in fuel cells [1,2]. Hydrogen gas is mainly produced from steam reforming of hydrocarbons, a large-scale, energy-intensive industrial process [3–5]. Photocatalytic water splitting has received considerable attention since it is an environmentally-friendly method for hydrogen production that does not form greenhouse gases [6]. However, oxygen is also generated and, therefore, the separation of the two obtained gases (hydrogen/oxygen) is required.

There is no commercial method for the H_2/O_2 separation although certain conventional technologies such as cryogenic distillation, pressure swing adsorption, or membrane technology can be considered [7]. Membrane technology is an attractive candidate because it involves simpler process schemes and is expected to have a lower operating cost [8], and has been demonstrated for conventional hydrogen separation [9]. Membranes for hydrogen purification are classified according to the composition of the selective layer. Dense polymer [10], porous ceramic [11], non-porous ceramic [12], porous carbon, graphene [13] and dense metallic membranes [14] are mostly used. The separation properties are shown in Table 1. As can be seen, these membranes require high operating temperatures which are not suitable for H_2/O_2 separation because of safety considerations.

Supported liquid membranes (SLMs) are promising materials for H_2/O_2 separations since they can be operated at room temperature. They consist of a porous support on which liquid is impregnated and they separate gases by the difference in solubility and diffusivity of each gas species in the liquid [15]. The supports decrease the thickness of the effective layer for gas separation and facilitate membrane handling, and can be used in various kinds of configurations such as flat sheets or cylindrical shapes.

Ionic liquid membranes (IL) are a subclass of liquid membranes which are widely studied for purification processes, especially for CO_2 separation [16–18]. Ionic liquids are stable due to their low volatility and show long lifetimes [19]. For example, the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) has been investigated for CO_2/N_2 separation, and it was suggested that its properties were influenced by the interaction with the membrane pore surface [20] and that immobilization of the liquid on the hydrophilic ceramic support was effective [21]. The influence of

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Table 1
Properties of hydrogen-selective membranes.

Membrane type	Dense polymer	Microporous ceramic	Porous carbon	Dense metalic
Temperature range (°C)	90–100	200–600	500–900	300–600
H_2 selectivity	< 10	10–1000	< 10	> 1000
H_2 permeance ($mol\ m^{-2}\ s^{-1}\ Pa^{-1}$)	$< 10^{-9}$	$\sim 10^{-7}$	$< 10^{-8}$	$\sim 10^{-6}$
Materials	Polymers	Silica, zeolite	Carbon	Palladium alloy
Transport mechanism	Solution-diffusion	Molecular sieving, site hopping	Surface diffusion, molecular sieving	Solution-diffusion

the temperature in the permeability of these gases through [Emim][Ac] is also described by an exponential Arrhenius type equation, with an activation energy that includes effects of diffusion and solubility [22]. It was found that the endothermic absorption offset the diffusivity and resulted in low activation energy.

The separation of H_2/O_2 using liquid membranes has been rarely investigated. Neves et al. [23] studied supported IL membranes (SILMs) to separate H_2, O_2, CO_2, N_2 and CH_4 at 303 K. Hydrophobic polyvinylidene fluoride (PVDF) was chosen as support material and 1-decyl-3-methylimidazolium tetrafluoroborate [C_{10}mim][BF_4] was used as ionic liquid. The obtained membrane had a H_2 permeance of $2.9 \times 10^{-10}\ mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ (estimated thickness was 125 μm) with a H_2/O_2 selectivity of 1.3. Gan et al. [24] fabricated SILMs using a nanofiltration membrane as support and [C4-mim][NTf_2] as the liquid. The authors measured the gas fluxes of H_2, O_2, N_2 and CO at various pressures. The maximum H_2 permeance was $2.1 \times 10^{-9}\ mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ and H_2/O_2 selectivity was 3.6.

Fluorocarbons can also be used in SLMs, and have been demonstrated for the separation of fluorinated hydrocarbons [25]. Our research group raised attention to a new type of application: gas separations. Perfluorocarbons (PFCs) are attractive candidates since they have high solubility for gases, high chemical stability and low vapor pressure [26], although reports of some cytotoxicity are of concern if direct contact with the fluids is made [27]. Castro-Dominguez et al. [28,29] investigated PFC-based SLMs using perfluorotributylamine (PFTBA) as liquid for the separation of H_2/O_2. The authors obtained a H_2 permeance of $1.0 \times 10^{-9}\ mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ with a H_2/O_2 selectivity of 140 measured at 313 K. They also applied the membrane for the separation of O_2/N_2 and achieved an O_2/N_2 selectivity of 60 measured at 313 K. Leelachaikul et al. [30] developed a PFC-based SLM for H_2/O_2 separation. Perfluorooctanol (PFO) was selected as a PFC. The obtained membrane had a H_2 permeance of $2.9 \times 10^{-10}\ mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ with a H_2/O_2 selectivity of 100 measured at 313 K. Though these PFC-based SLMs showed high selectivity [28–30], the obtained membranes had poor stability because of evaporation of the liquid.

The objective of this work is to obtain a supported liquid membrane with high performance and long lifetime. In order to evaluate the performance of membranes, the Robeson upper boundary was used [31], which shows a trade-off between permeance and selectivity and makes the comparison of the performance of membranes easy to visualize. This upper boundary for polymeric membranes gives a rapid indication of whether a membrane performs well or not. A recent technoeconomic analysis for various gas separations shows that there is an optimal point within the Robeson upper boundary for each gas combination [32]. Several parameters were investigated in order to improve the lifetime of PFC membranes such as PFC chemical structure and PFC amount. It was found that membranes which used 1H,1H,2H,2H-perfluorodecyl (PFDA) acrylate as liquid showed good performance beyond the Robeson upper boundary.

2. Experimental procedure

2.1. Materials

Porous alumina supports with inner diameter of 7 mm, outer diameter of 10 mm and average pore diameter of 60 nm were obtained from the Noritake Corporation. The perfluorocarbon-based liquids were soaked into the support and membrane thicknesses were calculated by the weight changes before and after soaking.

Dimethyl perfluorosebacate (DPFS, Wako Pure Chemical Industries, Ltd. CAS number 4590-24-3, Purity 95%), ethyl perfluorononanoate (EPFN, Tokyo chemical industry Co., Ltd. CAS number 30,377-52-7, Purity > 98%), 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA, Sigma-Aldrich, Co. LLC. CAS number 248-722-7, Purity 97%) and perfluoro(perhydrophenanthrene) (PPHP, Wako Pure Chemical Industries, Ltd., CAS number, 306-91-2) were selected as PFCs. The chemical structure and relevant physical properties for the investigated PFCs are shown in Table 2. Pure H_2, O_2 and Ar gases (purity > 99.9%) were obtained from Toatsu Yamazaki Co.

2.2. Membrane preparation

Porous alumina supports were connected to non-porous alumina tubes using glass seals which were fabricated by applying a glass paste and heating the joined pieces to 1273 K for 10 min with heating and cooling rates of $5\ K\ min^{-1}$. Then, the outer surface of the support was impregnated with a specific amount of PFC at room temperature. A micro-pipette was used for the manipulation and the amount of the impregnated liquid on the surface of the support was calculated by the weight difference of the membrane support before and after imbuing the liquid (Fig. 1).

2.3. Permeation test

The performance of the obtained PFC-based SLMs membranes was evaluated by measuring the permeance and calculating the pair-gas selectivity. The permeance was measured in a flow apparatus. The temperature during the gas separation was controlled using an electrical furnace (Fig. 2).

Both single and mixed gas permeance tests were carried out. In the single gas permeation test, the gases (H_2 or O_2) were diluted with Ar to make blends of H_2:Ar and O_2:Ar = 50:50 and were fed to the inner side. The flow rate for each gas was $25\ cm^3(NTP)\ min^{-1}$. In the mixed gas permeation test, H_2 and O_2 were introduced without Ar to the inner side of the membrane. The flow rates of H_2 and O_2 were each set to $25\ cm^3(NTP)\ min^{-1}$ to obtain the same partial pressures as with the single-gas measurements. Thus, the mixed gas composition was set to 50:50 even though the real application for photocatalytic water splitting creates H_2 and O_2 at a ratio of 67:33. Although the H_2:O_2 mixture of 50:50 was in the explosive regime, the volume of the unit was small and the membrane tube was mostly enclosed within the furnace.

In both types of measurements, the permeated gases were