Journal of Membrane Science 545 (2018) 176–184

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Effects of operating parameters and ionic liquid properties on fabrication of supported ionic liquid membranes based on mesoporous γ-Al_2O_3 supports

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ARTICLE INFO

Keywords:
γ-Al_2O_3 membrane
Supported ionic liquid membranes
Carbon dioxide capture
Hot coating
Controllable preparation

ABSTRACT

Supported ionic liquid membranes (SILMs) prepared with inorganic supports are more stable under high temperatures and differential pressures for gas separation than those based on organic membranes. In this study, a hot coating method was used to modify commercial α-Al_2O_3 tubular substrates to prepare high-quality membrane supports. Following impregnation of an ionic liquid (IL; [BMIM][BF_4] or [BMIM][Ac]) into the supports over a short time, the as-prepared SILMs were used for separation of N_2 and CO_2. The effects of preparation parameters, including impregnation time (0–1800 s) and impregnation temperature (18–59 °C) on SILM performance and IL loading were systematically investigated to gain a better understanding of the SILM preparation process. The optimum impregnation time was determined by considering both the permeance and the selectivity. Further, a high temperature was found to be beneficial for the preparation process because the viscosity of ILs is usually low at higher temperatures. However, when the viscosities of the two ILs ([BMIM][BF_4] and [BMIM][Ac]) were maintained at the same value by controlling the impregnation temperature, the qualities of the as-prepared SILMs were different, which may be due to the different surface tensions of these ILs.

1. Introduction

Nowadays, reducing greenhouse gas emissions is a great challenge for every country in the world. Among greenhouse gases, CO_2 has the greatest adverse impact on the greenhouse effect, causing approximately 55% of the observed global warming [1]. Supported ionic liquid membranes (SILMs) combine the low-energy consumption of membrane separation and the good absorbing capacity of ionic liquids (ILs) for CO_2 [2–6]. Compared with the traditional energy-intensive absorption method using alcohol–amine solutions, SILMs can avoid the loss of solvent via volatilization owing to the negligible vapor pressures of ILs. SILMs have attracted more and more attentions in the past 10 years [7,8]. Moreover, with a good choice of supports and ILs, SILMs could break the Robeson upper bound for CO_2/N_2 and CO_2/CH_4 separation [9,10], which shows their excellent potential for future applications.

In most of studies, organic membranes have been used as the supports for SILMs, which show permeabilities of 200–3000 Barrer with CO_2/N_2 selectivities of 10–70 [9,11,12]. However, the low strength and poor temperature resistance of organic membranes limit their applications at high temperatures and differential pressures (generally, < 150 °C and < 0.05 MPa). SILMs based on inorganic membranes (especially asymmetric tubular membranes) could overcome these disadvantages and maintain long-term stability in extreme conditions, and thus SILMs could be used in direct contact with flue gases [13–15]. Common inorganic membranes, such as SiO_2, TiO_2, and Al_2O_3, usually have high strength owing to the thickness of the substrates. In addition, the top layer, where IL is confined, is usually a mesoporous material that prevents the IL from being extruded under high differential pressures during gas permeation. Iarikov et al. prepared SILMs using an Al_2O_3 tubular membrane (average diameter of 5 nm) and [HMIM][Tf_2N]. These SILMs were stable for separation of CO_2/CH_4 at high pressures up to 0.4 MPa, which far exceeds the operating pressure of SILMs based on organic membranes (< 0.05 MPa). Vangeli et al. [15] prepared SILMs with SiO_2 tubular nanofiltration membranes (average diameters of 1 and 5 nm), which retained good performance and stability for CO_2/CO separation in the temperature range of 25–250 °C at differential pressures up to 0.5 MPa. In addition to the improvements in stability at high differential pressures and temperatures, another advantage of ceramic membranes is that the confinement effects of nanopores may greatly improve the separation efficiency. Labropoulos et al. [14] found that SILMs prepared with [BMIM][TCM] and 1 nm

Abbreviations: IL, ionic liquid; ILs, ionic liquids; EMIM, 1-ethyl-3-methyl-imidazolium; BMIM, 1-butyl-3-methyl-imidazolium; HMIM, 1-hexyl-3-methyl-imidazolium; Ph_3t, trihexyl(tetradecyl)phosphonium; BF_4, tetrafluoroborate; Tf_2N, bis(trifluoromethylsulfonyl)imide; TCM, tricyanomethanide; Ac, acetate

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http://dx.doi.org/10.1016/j.memsci.2017.09.071
Received 26 April 2017; Received in revised form 19 September 2017; Accepted 24 September 2017
Available online 27 September 2017
0376-7388/

Nomenclature

Latin

A	effective membrane area (cm^2)
d_p	pore size of the support (m)
E_p	activation energy for gas permeation through a SILM (kJ mol^{-1})
E_D	activation energy of gas diffusion in ILs (kJ mol^{-1})
ΔH_s	the partial molar enthalpy of gas absorption (kJ mol^{-1})
k_T	temperature coefficient
n	number of mole of gas in the chamber (mol)
p_2	pressure on the permeate side (kPa)
Δp	differential pressure between the feed and permeate sides (kPa)
Δp_I	differential pressure for impregnation (Pa)
P_a	gas permeance (GPU, 10^{-6} cm^3(STP) cm^{-2} s^{-1} $cmHg^{-1}$)
Q	gas flow rate (cm^3 s^{-1})
R	gas constant (kJ mol^{-1} K^{-1})
T	experimental temperature (°C)
T_0	temperature of the oven (°C)
t	experimental time (s)
t_I	impregnation time (s)
V_2	volume of the permeate side chamber (cm^3)
V_3	volume of the vessel V3 (cm^3)

Greek letters

α	ideal gas selectivity
δ	liquid height (m)
η	IL viscosity (Pa s)
σ	surface tension of IL (N/m)
θ	contact angle of the IL and the pore wall (deg)

SiO_2 tubular membranes had CO_2 permeabilities of 2–10 Barrer and CO_2/N_2 selectivities higher than 100. Moreover, they predicted the permeability by considering four important parameters, including the Henry constant, the gas diffusion coefficient in ILs, the porosity, and the tortuosity of the supports. All these parameters were determined experimentally, and they found the experimental permeability to be about 10 times larger than the theoretical value. They pointed out that randomly oriented $[BMIM]^+$ became well aligned under the confinement effect of the nanoscale pores, which reduced the gas permeation resistance.

However, the high permeabilities of ceramic-based SILMs do not translate into competitive permeances, as the thickness of the stabilized liquid is large compared with that of the active film in an asymmetric membrane [16]. Excessive ILs are impregnated into the support relative to the actual amount required for the support's active film, mostly to prevent the appearance of “pinholes” and improve the gas selectivity. For instance, Labropoulos et al. [14] prepared asymmetric-inorganic-membrane-based SILMs by a vacuum-assisted liquid infiltration technique, which resulted in a liquid membrane that of 20–39 μm thick, while the active layer of the support was only 1.52 μm thick. Even though the CO_2/N_2 selectivities of the SILMs were higher than 100, the CO_2 permeances were smaller than 0.27 GPU. Albo et al. [13] used a coating method to prepare [EMIM][Ac]-based SILMs, using an inorganic asymmetric membrane with a super thin TiO_2 mesoporous layer. The obtained SILMs exhibited a CO_2/N_2 selectivity of 30 with high CO_2 permeances up to 120 GPU. Their work sheds light on the use of inorganic asymmetric membranes to improve the permeance of SILMs.

Nevertheless, there are only a few reports focusing on preparation methods for inorganic-support-based SILMs, and studies on preparation parameters, such as impregnation time and temperature are scarce.

In this work, a hot-coating method [17] was used to modify commercial mesoporous γ-Al_2O_3 supports to obtain thin, perfect intermediate and top layers. Then, SILMs were prepared by impregnating ILs into the supports within a short time. The effects of preparation parameters, including impregnation time and impregnation temperature, were systematically studied to obtain a better understanding of the SILM preparation process. In addition, the influence of IL viscosity on the qualities of the prepared SILMs, such as the CO_2/N_2 selectivity and IL loading, was examined by controlling the impregnation temperature or varying the type of IL. Finally, the effects of permeation temperature and differential pressure were also investigated to improve the understanding of the separation performance of SILMs.

2. Experimental

2.1. Materials

The ILs used in this study were 1-buthyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-buthyl-3-methylimidazolium acetate ([BMIM][Ac]) provided by Shanghai Cheng Jie Chemical Co. Ltd. (purity > 98%) and used with no further purification. Commercial α-Al_2O_3 tubular ceramic substrates were obtained from Jiexi Lishun Science and Technology Co. Ltd. The average pore diameter of the substrates was 2.0 μm and the maximum defect was smaller than 2.9 μm, as confirmed by the bubble pressure method [18]. The α-Al_2O_3 particles (AKP 53, average diameter of 0.2 μm) was supplied by Sumitomo Chemical Co. Ltd. Aluminum isopropoxide, Eosin Y disodium salt, and Cyclohexane were of analytical grade and supplied by Sinopharm Chemical Reagent Co. Ltd. N_2 and CO_2 with purity of 99.999% were provided by Dalian Gas Co. Ltd.

2.2. Preparation and characterization of γ-Al_2O_3 supports

The commercial α-Al_2O_3 tubular had outer and inner diameter of 12 and 8 mm respectively, with a length of 200 mm, porosity of 38% and average pore size of 2.0 μm. The substrate was cut into several pieces, each with a length of 50 mm. Because of their large pore diameter, the commercial α-Al_2O_3 tubular ceramic membranes could not be used directly as supports for the SILMs. The hot coating method [17,19] was used to prepare γ-Al_2O_3 supports on the α-Al_2O_3 substrates. Firstly, a mixture of BS40 (boehmite sol with an average particle size of 40 nm [20]) and 5 wt% α-Al_2O_3 particles (commercial, average particle size of 200 nm) was coated on the hot commercial α-Al_2O_3 tubular substrate (170 °C), which was then directly subjected to thermal treatment at 500 °C for 20 min to prepare the intermediate layer. The hot-coating and thermal treatments were repeated 7 times. To prevent the occurrence of cracks, the mixture of BS40 and α-Al_2O_3 particles was gradually diluted with deionized water, and the concentrations of the mixture for the 1–2, 3–5 and 6–7 coating processes were 100%, 50%, and 25% of the original mixture, respectively. Secondly, the BS40 sol was coated on the intermediate layer to prepare a mesoporous γ-Al_2O_3 top layer using the same process as described above, while the coating and thermal treatment process were repeated 10 times. The sol concentrations for the 1–2, 3–6 and 7–10 coating processes were 100%, 50% and 25% of the original BS40 sol, respectively.

The pore size distribution of the as-prepared support was determined by the permporometry method [21]. The pore size was calculated according to Cao's work [22], in which the t-layer was considered. The t-layer is the layer of molecules (cyclohexane in this work)