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Water vapor permeation and dehumidification performance of poly (vinyl alcohol)/lithium chloride composite membranes



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ABSTRACT

Thin and robust composite membranes comprising stainless steel scaffold, fine and porous TiO₂ and polyvinyl alcohol/lithium chloride were fabricated and studied for air dehumidification application. Higher hydrophilicity, sorption and permeation were observed for membranes with increased lithium chloride content up to 50%. The permeation and sorption properties of the membranes were investigated under different temperatures. The results provided a deeper insight into the membrane water vapor permeation process. It was specifically noted that lithium chloride significantly reduces water diffusion energy barrier, resulting in the change of permeation energy from positive to negative values. Higher water vapor permeance was observed for the membrane with higher LiCl content at lower temperature. The isothermal air dehumidification tests show that the membrane is suitable for dehumidifying air in high humid condition. Additionally, results also indicate a trade-off between the humidity ratio drop with the water vapor removal rate when varying air flowrate.

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1. Introduction

The use of membranes for isothermal dehumidification processes has vast applications in a wide array of industries including heating, ventilation and air conditioning (HVAC) [1,2]; dehydration of flue gas [3–5], natural gas [6,7] and organic vapors [8,9]; drying of compressed air [10], steam recovery [9] and air treatment for packaging and processing industries.

Humid air or gas can be dried when it goes through the isothermal filtration setup [1,11–13] as shown in Fig. 1. In this setup, a permselective membrane is sandwiched between two chambers. One chamber is continuously fed with a stream of humid supply air. The other chamber is connected to a vacuuming system to produce a transmembrane pressure which acts as a driving force for the filtration process [1,11,12,14]. When the humid air stream passes along the membrane, the water vapor is selectively and efficiently sieved out. As a result, the air becomes dried without any change in its temperature [11–13,15].

The operation of the dehumidification system relies largely on the mechanical and permeation properties of the working membrane. Most of the membranes thus far have been constructed in a composite structure comprising support layers and an active layer [6,13,14,16]. The support layers provide the high mechanical

strength and eventual chemical stability to the membrane. They are usually made of porous materials which have high permeability but no selectivity. The active layer is a thin permselective layer which determines the permeability and selectivity of the whole composite membrane. Composite membranes have higher permeability and mechanical strength than single-layer membranes with the same thickness. Therefore, the development of inexpensive and high performance composite membranes has attracted much research interest in the field of isothermal air/gas dehumidification [1,6,12–14,16].

Thus far, hydrophilic polymer [1–3,6,8,12,17–19], ceramic materials [13] and liquid membranes [14,16,20–22] have been widely used for membrane active layer. Among them, hydrophilic polymer has attracted much attention due to its high water permeability and selectivity [2,4,6–8,12,17–19,23–26]. These are usually dense membranes for which water vapor transfer is based on solution-diffusion mechanism. Water molecules absorb on the membrane surface, diffuse through the membrane and then desorb at the opposite surface [25–27]. Transfer parameters such as permeance and selectivity are dictated by the membrane solubility and diffusivity properties. PVA polymer has been one of the popular choices of material for these membranes due to its hydrophilic properties, stability and ease of film formation [2,8,12,19,23,24,28]. The modification of PVA using lithium chloride to enhance water permeability has been reported [12,19]. The change of the polymer structure by including LiCl has been studied by means of FT-IR, XRD and thermal analysis [19,29]. LiCl salts disperse into the PVA matrix and

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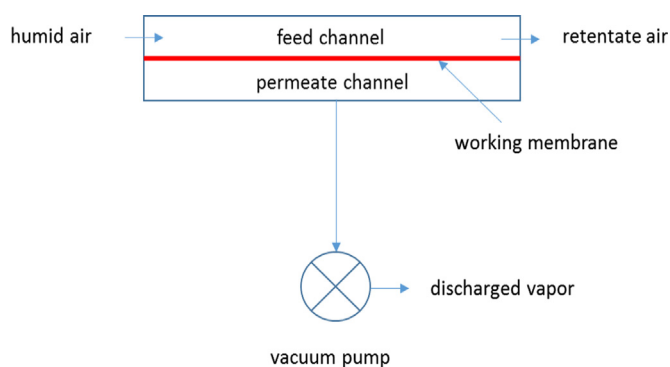


Fig. 1. Dehumidification test setup.

weaken the hydrogen bonds between PVA chains. A complex formation was proposed between LiCl and PVA [29] with Li ions being the center cations and are weakly bonded with the oxygen atoms residing within the PVA molecules. As a result, the crystallinity of the PVA decreases with the higher LiCl contents. However, there are a lack of detailed research works on the analysis of the energies associated with water sorption and diffusion processes and how they affect the resultant water permeation. Therefore, the permeation mechanism of polymer membrane is still an area with a lot of potential for exploration.

Recently, we have developed an inexpensive, thin and highly stable metal-supported hydrophilic polyvinyl alcohol (PVA)/lithium chloride (LiCl) composite membranes using the dip-coating method [12]. In that study, experimental and modeling analyses were carried out to evaluate the performance of a vacuum membrane dehumidification system. In this study, the fundamental aspects of the water permeation, sorption, and diffusion energies are extensively studied to elucidate the role and influence of LiCl on the water transport phenomena in the membrane material. The study provides an in-depth understanding of the membrane permeation mechanism including the tailoring of the membrane properties for specific applications. The membranes were then tested in an isothermal filtration setup specially designed for air dehumidification.

2. Experimental

2.1. Membrane preparation

Anhydrous lithium chloride and polyvinyl alcohol (99% hydrolyzed, molar weight of 85,000–124,000) were procured from Sigma Aldrich. Fine and porous TiO₂ (Degussa P25) was obtained from Evonik Industries AG and used without further modification. Stainless steel mesh with twilled dutch weave and 5 μm aperture was used as the scaffold.

A 5 w% TiO₂ suspension solution was prepared by adding P25 TiO₂ to distilled water and subjected to vigorous stirring. PVA solutions were prepared by dissolving PVA in distilled water to form 5 w% solution under constant stirring at 90 °C. LiCl was then accordingly added to the PVA solution and stirred at room temperature for 2 h to obtain solutions with different PVA/LiCl mass ratios of 1:0 (PVA only), 5:1, 2:1, 3:2 and 1:1, corresponding to 0%, 16.7%, 33.3%, 40% and 50% LiCl content respectively.

The stainless steel scaffold was dip-coated in the TiO₂ suspension solution and then dried at 80 °C for 10 min. The dipping and drying were repeated 10 times until an even white TiO₂ layer covers all the mesh holes on both sides. The mass of the TiO₂ layer was obtained to be 5 mg/cm². The formed membranes were then dipcoated in the PVA/LiCl solutions and dried at 80 °C for 10 min.

Multiple layers were dipcoated and dried alternately to obtain a uniform selective layer with desired permeation properties. The mass of the polymer layer with 5 polymer dips was measured to be 5 mg/cm².

2.2. Membrane characterizations

The membrane morphology was observed through the scanning electron microscope (SEM). The hydrophilicity of the membrane surface was tested by contact angle measurements using KINO SL150 with measuring accuracy of ±0.1°. For each membrane, the contact angle reading was taken as the average of five equally spaced out points on the membrane.

The water vapor permeation properties of the membranes were estimated based on the cup method. The membrane with an area of 33 cm² was mounted on the opening of a test cup. The test cup was fully filled with dried silica gel to minimize the resistance of still air gap between silica gel and membrane. The test cup was placed in a humidity and temperature chamber so that the humidity difference between the two sides of the membrane was precisely controlled. The air inside the chamber was vigorously circulated with a strong air displacement fan to minimize boundary layer resistance on the outer side of the membrane. The accuracies of temperature and relative humidity are ±0.2 °C and ±1%, respectively. Water vapor permeance (*P*) was obtained from the weight increase of the test cup [12,30]. To study the effect of temperature, the water vapor permeations of the membranes were measured at different temperatures, assuming that the sorption property of silica gel was unchanged. From the obtained result, the water vapor permeation energy was determined.

Air permeance measurements were conducted according to the ISO 15105-1 standard. The membrane was mounted on a gas transmission cell so as to form a sealed barrier between two chambers. Both chambers were evacuated. Dry air was then introduced to one chamber and the pressure in the other chamber was monitored over time. The air permeation through the specimen was determined based on the pressure change [12]. Pressure measuring resolution of 1 mbar. It was reported that N₂ permeability is independent of water content in feed gas [3,17]. Therefore, the water vapor selectivity toward air can be estimated by the ratio of water vapor permeance to air permeance.

Water vapor sorption of the mixtures of PVA and LiCl were studied using Quantachrome Aquadyne DVS gravimetric dynamic vapor sorption analyzer. The water sorption capacity (*C*) is defined as

$$C = \frac{m_e - m_0}{m_0} \cdot 100\% \quad (1)$$

where, *m_e* and *m₀* are masses of the sample at water absorption equilibrium and dry states, respectively. The effect of temperature on the sorption property of the material was studied, and then the sorption energy was determined. Gravimeter, relative humidity and temperature accuracies are ±1 μg, < ±2% and ±0.2 °C, respectively.

The dehumidification performance was tested in an instrumented experimental setup shown in Fig. 1. A flat sheet membrane with an area of 20 cm² was mounted between the two chambers-feed and permeate channels. Geometry of both permeate and feed channels is W20xL100xH2.5 mm [12]. Permeate channel was connected to a vacuum pump. Permeate pressure was set at 1 mbar and monitored by a pressure gauge (Omega DPG1000B, accuracy < ±0.35%). In the feed channel, an inlet humid air with relative humidity (RH) of 90% and humidity ratio of 17 g water vapor/1 kg air was passed over the membranes at room temperature of 24 °C. The flow rate of the inlet air was controlled using a suction pump and a Kobold KFR2113N0 flow meter with

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