Fixed-site-carrier facilitated transport of carbon dioxide through ionic-liquid-based epoxy-amine ion gel membranes

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ABSTRACT

The amine functional groups in room-temperature ionic liquid (RTIL)-based epoxy-amine ion gel membranes allow for the fixed-site-carrier facilitated transport of CO_2. These membranes were tested under humidified mixed-gas (CO_2/N_2) feeds in order to evaluate the effects of relative humidity, CO_2 partial pressure, and hydrophobicity of the added free RTIL on CO_2/N_2 separation performance. Changes in relative humidity were found to have little effect on CO_2/N_2 separation performance at constant CO_2 partial pressure. However, comparison to dry-gas measurements showed that the presence of water vapor is necessary to observe facilitated CO_2 transport in these systems. Increased CO_2 permeability and CO_2/N_2 selectivity were observed for these epoxy-amine ion gel membranes with decreasing CO_2 partial pressure, as expected for materials operating via the fixed-site-carrier facilitated transport mechanism. The hydrophilicity of the free RTIL was found to influence CO_2 transport, with a more hydrophilic RTIL able to facilitate CO_2 transport at lower relative humidity. Facilitated transport enhances the CO_2/N_2 separation performance of these epoxy-amine ion gel membranes and enables them to exceed the 2008 Robeson plot upper bound.

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1. Introduction

Carbon dioxide (CO_2) gas accounts for roughly 80% of anthropogenic greenhouse gas emissions and has been associated with both global climate change and ocean acidification [1]. To mitigate the unavoidable environmental consequences related to these phenomena, it is desirable to prevent or limit atmospheric CO_2 emissions from large point sources, such as coal and natural gas-fired power plants. This can be achieved by post-combustion carbon capture and sequestration (CCS). CCS involves the capture, and purification of CO_2, followed by sequestration and/or utilization of the captured CO_2 [2].

The first step in post-combustion CCS technology requires an inexpensive, large-scale method of separating CO_2 from the other light gases present in flue gas (primarily N_2) [2,3]. Conventional technologies to separate CO_2 from flue gas streams include amine adsorption, cryogenic separations, pressure swing adsorption, and membrane separations [4]. Polymeric gas separation membranes offer the relative advantages of low operating and capital costs, ease of operation, and modularity, due to their smaller size [5,6]. For these reasons, there has been considerable scientific and industrial effort to design and develop polymeric membrane materials for post-combustion CCS.

Gas transport in dense polymer membranes proceeds via the solution-diffusion transport mechanism. Gas molecules transport across a partial pressure gradient by dissolving at the upstream (feed) interface, diffusing through the membrane and desorbing at the downstream (permeate) interface [7,8]. All polymers have an inherent gas permeability and selectivity. Gas permeability is defined as the gas flux, normalized to the membrane thickness and transmembrane pressure difference. Gas selectivity is the ratio of the permeability of the faster gas species through the membrane to that of the slower gas penetrant [7].

For polymer membranes, a permeability – selectivity trade-off is typically observed, (i.e., as polymers become more permeable they also become less selective). This trade-off is represented by the empirically-derived Robeson upper bound, which has been explained by Freeman [8–10]. In general, a membrane material with permeability – selectivity behavior close to or above the CO_2/N_2 upper bound has excellent separation potential for post-combustion CCS. A major

challenge for membrane-based CO_2 separation is to produce membranes with both high CO_2 permeance and high CO_2/N_2 selectivity in order to compete with traditional separation technologies [5].

Room-temperature ionic liquid (RTIL)-based materials have been explored for CO_2/N_2 separations because of their negligible vapor pressure, inherently good CO_2/light gas solubility selectivity, and high CO_2 diffusivity compared to most polymer membranes [11,12]. RTIL-based ion gels are defined as solid–liquid composite materials that utilize cross-linked, polymerized room-temperature ionic liquids (poly(RTIL)s) to physically entrap added free RTIL [13–16]. Many groups have investigated the formation RTIL-based ion gels because the free, "unbound" RTIL provides advantageous gas diffusivity while maintaining the mechanical properties of a solid material [13–15,17–19]. Many RTIL-based membranes have permeability-selectivity performance for CO_2/N_2 separation that lies near or above the 2008 Robeson upper bound [13–17,20]. Therefore, these materials are promising candidates for preparing high-performance membranes for CCS [21].

Facilitated transport refers to a transport mechanism that can occur in conjunction with the solution-diffusion mechanism [22]. Facilitated transport operates by either "mobile" or "fixed-site" carriers, which are chemical functional groups capable of a reversible chemical interaction (chemical or physical) with a specific gas molecule (e.g., the reversible reaction of amines with CO_2). Relevant to this work are fixed-site-carrier facilitated transport membranes, in which the interactive/reactive carrier groups are fixed (i.e., covalently bonded) to the membrane [23–25].

Fixed-site-carrier facilitated transport of CO_2 has been reported for many different membrane compositions [26–30]. Amine-containing polymers and small molecules are the most common CO_2 carriers. Humidified, mixed-gas permeation tests are generally required to effectively evaluate whether or not facilitated transport occurs in these membranes. The role of humidification (i.e., presence of water vapor) for the amine-facilitated transport of CO_2 is depicted in Fig. 1 [31,32]. Reactions 1–4 in Fig. 1 make up the zwitterion mechanism in which water acts as a co-reagent with primary ($1°$) or secondary ($2°$) amines to react with CO_2 [33]. CO_2 first reacts with either a $1°$ or $2°$ amine to form a zwitterion intermediate (reaction 1). The zwitterion is then deprotonated by another amine or H_2O to form a carbamate salt (reactions 2 and 3). Lastly, the carbamate ion can react with H_2O to form bicarbonate, (HCO_3^-). CO_2 transport can be facilitated in the form of bound carbamate and HCO_3^-. Lastly, the presence of tertiary ($3°$) amines can facilitate the transport of CO_2 via reaction 5, wherein CO_2 and H_2O react with a $3°$ amine to form ammonium and HCO_3^-.

Facilitated transport operates when the carrier concentration in the membrane is similar to the solute concentration in the gas feed. At higher solute concentrations, the carrier sites become saturated, and the solution-diffusion mechanism dominates. At low solute concentrations, facilitated transport can occur and results in enhanced transport behavior. This non-linear transport behavior with solute concentration is an identifying feature of facilitated transport [22]. Since the CO_2 content in post-combustion flue gases is low (4–10% for natural gas-fired, and ~13% for coal-fired power plants, respectively) and contains water vapor, the facilitated transport mechanism has great potential for this separation.

Our group recently reported the use of epoxy-amine chemistry to prepare ion gel membranes containing up to 75 wt% free RTIL (Figs. 2 and 3) [15,16]. These materials possess amine functional groups in the poly(RTIL) matrix and have high CO_2 solubility under ideal (dry, single gas) conditions. These amine functional groups should also allow for fixed-site facilitated transport of CO_2 to occur [26–30,34]. Compared to conventional materials used for fixed-site-carrier facilitated transport, epoxy-amine ion gel membranes have higher ideal CO_2 permeability [15,16,27,34–36].

To our knowledge, there have been no previous literature reports of fixed-site-carrier facilitated transport in RTIL-based ion gel
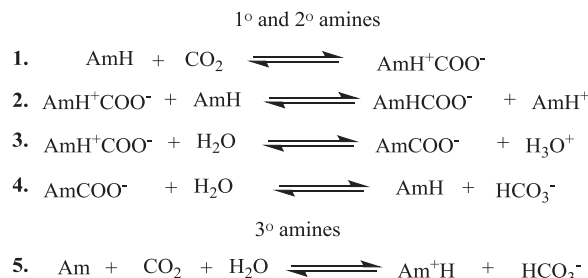

Fig. 1. The typical reactions that occur between amines (Am) with CO_2. CO_2 transport can be facilitated by either the bound carbamate or the bicarbonate ion.

membranes. In this study, we report the observation of facilitated transport in epoxy-amine ion gel membranes. Humidified, mixed-gas feed streams were used to evaluate the key parameters of relative humidity (RH), CO_2 partial pressure, and the relative hydrophobicity of the added free RTIL on the CO_2/N_2 separation performance. Herein, we show that water vapor is necessary to observe facilitated transport in RTIL-based epoxy-amine ion gel membranes; that the CO_2 permeability and CO_2/N_2 selectivity of some epoxy-amine ion gel membranes increases with decreasing CO_2 partial pressure, indicative of facilitated transport; that a more hydrophilic free RTIL results in larger enhancements in CO_2/N_2 separation performance; and that higher amounts water vapor and higher amine loading are necessary to observe facilitated transport when a hydrophobic RTIL is used. The CO_2/N_2 separation performance of these systems falls near or above the 2008 Robeson upper bound.

2. Experimental

2.1. Materials and instrumentation

Helium, CO_2, and N_2 gas cylinders were purchased from Airgas (Randor, PA) with gas purities of $\geq 99.99\%$. Omnipore™ (porous poly(tetrafluoroethylene) (PTFE), average pore size 0.2 µm, and 80% porosity) membrane filters were purchased from EMD Millipore. Hydrophobic PTFE membrane filters were purchased from Advantec (cat. no. T020A047A, average pore size 0.2 µm, and 74% porosity). ^1H and ^{13}C NMR spectra were acquired using a Bruker Avance-III 300 spectrometer. Membrane thicknesses were measured with a digital micrometer. FT-IR spectra were obtained using a Nicolet 6700 FT-IR spectrometer in attenuated total reflectance (ATR) mode. A Hewlett Packard 5890 gas chromatography instrument equipped with a HayeSep D column and a thermal conductivity detector was used to analyze the feed and sweep stream compositions for the mixed-gas permeation studies. The membrane materials displayed in Fig. 2 were synthesized as previously described in the literature, and their characterization and purity data agree with those reported [12,14,15,37].

2.2. Mixed-gas permeation tests

Fig. S1 in the Supporting Information displays a schematic of the mixed-gas permeation system used in this study. A membrane area of 11 cm^2 was used for the permeation tests. The active membranes were placed on top of a hydrophobic PTFE filter to provide additional support and prevent RTIL contamination in the system [20]. The feed flow rate was held at either 50 or 100 cm^3 (STP)/min, and the sweep flow rate was held at 7 cm^3 (STP)/min. All measurements were collected at room temperature with a feed pressure of 102 kPa and a sweep/permeate pressure of 85 kPa. The membranes were allowed to equilibrate for at least 3 h after changing any experimental parameter to ensure data was collected under