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Water Transmission Mechanisms in Advanced Ionic Membranes for HVAC Applications

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Abstract

Ionic membranes are widely used in the electrochemical applications such as electrolysis and fuel cells. Recent advances in these membranes have led to new markets for ionic membranes, that can provide high water permeability in heating, ventilation, and air conditioning (HVAC) applications. These materials can be useful in many applications to help provide more efficient building technologies and higher indoor air quality through devices such as ionic liquid heat pumps (ILHPs), ionic liquid desiccants (ILDs), and energy recovery ventilators (ERVs) and water-based evaporators (WBEs). Water transmission mechanisms behind the water transport is not well understood, since different functional membranes provide transmission in different ways. Water transportation can be a function of ionomer structure via the building blocks of the backbone, or from the functional groups on the side chains or from subtle features in membrane design and composition. In this work, we studied the permeation properties of different advanced ionic membranes. Membranes that show high water selectivity, and permeances exceeding $4 \times 10^5 \text{ g}/(\text{day} \cdot \text{m}^2 \cdot \text{Pa})$ are presented. Principal mechanisms driving the water transmission such as sorption, diffusion, and pervaporation (permeation/evaporation) are described and identified for different classes of membranes. High performance membranes are identified for optimum applications for different HVAC systems.

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Keywords: Moisture Transmission; Membranes; Ionomer; ERV; Ionic Liquid

1. Introduction

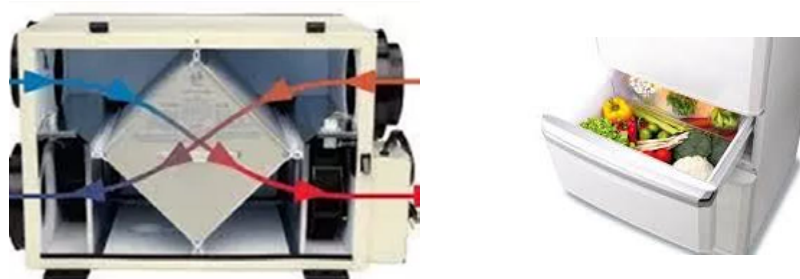
The number of air conditioning units employed globally will increase from approximately 1.2 billion units to at least 4.5 billion by 2050. Developing countries will see a fivefold increase in demand over the same period. This increased demand will place a massive new burden on electricity grids that are already straining under current demand. When combined with the atmospheric impact of the refrigerants utilized by air conditioners, the energy consumption associated with mechanical cooling represents one of the largest end-use risks to our climate. Hence heating and cooling for buildings is accounts for a good portion of the resource demand in the developed world. Sustainable and high efficiency technology for heating and cooling applications is critical global need.

Water transporting membranes can be useful in many HVAC applications that reduce the total energy load for buildings. In one application, this is done by reducing the relative humidity in the air to be treated (and reduction in latent heat requirements in HVAC systems). Ionic liquids, as the name implies, are ionic salts that remain liquid under normal operating conditions. These fluids are mainly useful for their desiccation properties as concentrated ionic liquids (ILD's), as they can adsorb or desorb water vapor to help control the relative humidity of the air in its container. With membranes, they are mainly utilized in flat sheet or shell and tube contactors that utilize fluid flows of air and desiccant in crossflow patterns. These systems can dehumidify gas streams with high efficiency. Additionally, these contactors can be paired with a heat pump system to

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regenerate the desiccant so that the system can be operated in a loop. In Energy recover ventilator (ERV) applications, an assembly of membranes allows exchange of heat between a cool and warm airstream (incoming and outgoing streams required to make up fresh air in buildings). In yet another application, membranes are used to enable heated water from heat pump systems to evaporate. Membranes in all these applications allow water vapor to transport from one side to the other. Interestingly, these classes of membranes are also being used to control humidity in vegetable trays in refrigerators. There are many other critical applications like for example sea water desalination membranes where water transmitting membranes have utility. Thus, the transport rate of water in membranes is clearly a critical issue in the performance of these systems. This paper provides basic insight into water transmission across functional (non-porous) membranes.

Figure 1 & 2. Applications for Advanced Ionic Membranes



It should be noted that there are two classes of membranes used for these applications, porous and non-porous membranes. Porous membranes are typically microporous structures with 'open' pores which allow for gas flow across the membranes; while non-porous membranes typically involve impervious polymer films that do not allow any bulk (gas) flow across them. There are significant differences in how these two classes of membranes perform. Micro-porous membranes generally offer higher water transmission rates, but also allow bulk flow (i.e. contaminants) to also cross the membranes. Impervious (non-porous) membranes offer much higher selectivity, however with some reduction in water transmission rates. This paper only reviews impervious non-porous membranes, which are targeted at applications that require no, or low cross contamination; and usually very long operating life. These applications include ERV's where contamination of incoming air into a building is a critical issue, and in ILD's where salt carryover, and salt crystallization in micro-porous membranes is also a critical issue in operation.

Polymeric, non-porous reinforced membranes made from (ionically) functionalized polymer materials that transmit water were originally developed as solid polymer electrolytes for electrochemical applications [1]. These materials were originally developed as solid polymer electrolytes for electrochemical applications. These materials typically have ionically conductive groups embedded in the repeating unit of the polymer. These functional groups aid in the transport of water through the membrane.

Water mass transfer mechanisms are reviewed, different transport mechanisms are discussed, and performance data is provided for reference.

2. Water Transmission Mechanisms

Water transmission mechanisms behind the water transport is not well understood, since different functional membranes provide transmission in different ways. Water transportation can be a function of

ionomer structure via the building blocks of the backbone, or from the functional groups on the side chains or from subtle features in membrane design and composition.

2.1. *Electro-Osmotic Drag*

When a voltage is applied across the polymer electrolyte membrane, water is mainly transported inside the membrane by electroosmotic drag. Fig. 3 is a schematic of the water transport in a fuel cell membrane. The two main water transport processes in the membrane are electro-osmotic drag and back diffusion. Electro-osmotic drag refers to the phenomenon of water molecules being dragged by the current-carrier protons from the anode to the cathode. The electro-osmotic coefficient is the transport number of water molecules that are carried with each proton moved from the anode to the cathode. The electro-osmotic coefficient mainly depends on the temperature and water content.

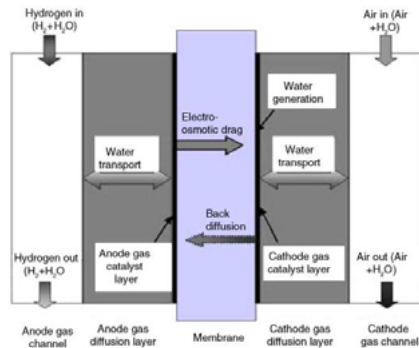


Figure 3: Schematic of water transport in a proton exchange membrane (PEM) fuel cell

2.2. *Solution-Diffusion Theory*

Solution-diffusion is the generally accepted mechanism of mass transport through non-porous membranes, which was first proposed by Graham [1] based on his extensive research on gas permeation through homogeneous membranes. It is held that gas permeation through a homogeneous membrane consists of three fundamental processes: (1) solution of gas molecules in the upstream surface of the membrane. (2) Diffusion of the dissolved species across the membrane matrix. (3) Desorption of the dissolved species in the downstream face of the membrane. These three fundamental processes also govern the mass transport across pervaporation membranes [2]. A schematic of the solution-diffusion theory is as shown in Fig. 4.

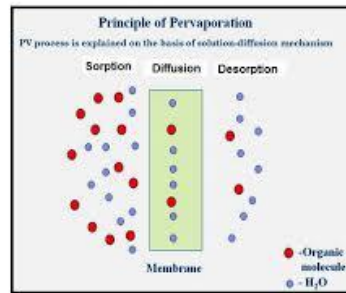


Fig. 4. Schematic of Solution-Diffusion in Pervaporation

It is to be noted that the solution-diffusion theory is only valid for governing permeation through non-swollen membranes. If membranes are swollen or plasticized by transporting species, the interactions between polymer chains tend to be diminished, and the membrane matrix will therefore experience an increase in the free volume. Hence, to reflect the permeation the solution-diffusion must be modified to account for the increase in the free volume. In the next section we discuss the results obtained from ASTM E96 and MDM testing.

2.3. Pervaporation

Pervaporation (permeative evaporation) is a mass transport phenomenon present in dense non-porous membranes. Pervaporation occurs in a gas-liquid separation system that is separated by the membrane, as the liquid contacts the membrane surface it permeates and undergoes a liquid to vapor phase change to end up in the gas stream. This can be done in reverse to remove a gas vapor to the liquid phase, as would be done in an ILD system. There are two main models that are used to describe the transport process: Free Volume and Diffusion; the latter being the more common. However, both models are important to understand and may describe the systems better in cases discussed below.

The free volume model describes a system where vapor passes through a membrane from a high concentration feed to a low concentration permeate stream. This low concentration can be established by using a vacuum line or a condenser, but the driving force is established by the difference in partial pressures between the two feeds. The mass flux is established through corresponding adsorption-desorption processes on the corresponding faces of the membrane. This flux can be established by using a condenser downstream on the permeate side, and it can be increased by adding a heater to the feed stream. These units would create the pervaporation process in the combination of the adsorption and corresponding desorption of the liquid within the membrane, and the evaporation of the liquid from the surface of the membrane with partial pressure differential. This model for membrane flow is more useful in porous materials such as fiberglass or expanded polytetrafluoroethylene membranes like those commonly used in air conditioners [3], [4].

For non-porous membranes the model must include a mechanism for the diffusion of the pervaporate through the solid structure of the polymer. The solution-diffusion is defined by Fick's laws of diffusion. Fick's first law defines the flux of the system to be proportional to the concentration gradient of the fluid. This law is represented mathematically as Equation 1, where J is the flux of the system, D is the diffusion coefficient, ϕ is the concentration of the molecule to be dissolved, and x is the one-dimensional distance. This law describes the molecular movement of molecules from areas of high concentration to low. Fick's second law describes the diffusion dependence of the concentration gradient with respect to time. This law is derived from the first law's interaction with the law of mass conservation. The equation can be written as Equation 2. This is useful for non-steady state systems such as the air conditioning cycle. The diffusion coefficient will change based on the conditions of the system. The predominant variables are temperature, viscosity, and density. For polymer systems the diffusion coefficient can also be dependent on the primary on the concentration of the molecule within the membrane itself. This permeate in polymer is known as swelling and can have both positive and negative effects on the pervaporate and mechanical performance of the membrane [5]. Additionally, this can make real systems significantly more complicated as the change in concentration can create a change in membrane thickness [1], [3-5], [6].

$$J = -D \frac{d\phi}{dx} \quad (1)$$

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \quad (2)$$

The driving force for transport of different components is provided by a chemical potential difference between the liquid feed/retentate and vapor permeate at each side of the membrane. The retentate is the remainder of the feed leaving the membrane feed chamber, which is not permeated through the membrane. The chemical potential can be expressed in terms of fugacity, given by Raoult's law for a liquid and by Dalton's law for (an ideal) gas. During operation, due to removal of the vapor-phase permeate, the actual fugacity of the vapor is lower than anticipated on basis of the collected (condensed) permeate.

For many systems, ionically functionalized polymers are proving to be the most exciting developments. These systems are made from standard polymer backbones that could be functionalized with sidechains capped with an ionic group. These chains can be of varying length and the caps are of strong acids or bases. The most well-known of these is perfluorosulfonic acid (PFSA), which consists of a backbone of polytetrafluoroethylene with an end capped with a sulfonic acid group. This ionomer is both temperature and chemically stable. Other ionomers are functionalized with trimethylammonium, pyridine, or imidazole groups as well. The ionic groups significantly aid these materials in their water transport properties due to their hydrophilic nature. However, research in recent years indicates that the ionic groups form ionic channels formed by areas of clustered functional groups. These channels form ordered pathways for the water to more easily transfer from one surface

of the membrane to the other that are more thermodynamically favorable than the simpler diffusion seen a homopolymer with a hydrophilic backbone. These micro- or nanostructures can be aided with the addition of a surfactant or a scavenger [2], [7], [8].

Pervaporation was mainly studied and used for organic solvent dehydration. Several hydrophilic and hydrophobic membranes have been used for this application. However, hydrophobic membranes work for these purposes by selectively allowing organic compound to pass through while rejecting water and they cannot be used for HVAC applications since the membranes need to permit water movement at high flux rates. There are several available commercial polymer membranes such as polyurethanes (PU), polyvinyl alcohol (PVA), polyimides (PI), Sulfonic Acid functionalized polymer (Perfluoro and Polystyrene i.e. PFSA's and PSSA's) and polyacrylonitrile (PAN) [9].

Water transport in PFSA membranes has been studied extensively in relation to their use in electrochemical devices (such as fuel cells and electrolysis applications). In PFSA's water transport proceeds through a combination of diffusion through void spaces in the membrane, along with protons through the pores in the membrane due to electro-osmotic drag and hydraulic permeation due to pressure gradient [10]. Sulfonated styrene/ethylene – butylene/styrene (S-SEBS) triblock polymer is another low-cost proton conducting material. The sulfonic acid functional group is connected to the backbone via a fluorocarbon sidechain in PFSA's and via a benzene ring in S-SEBS [11]. The hydrophilic and hydrophobic regions in both these materials show microphase separation as seen in Figure 5, forming narrow channels through which proton and water transport takes place. In the left of Figure 5, the hydrophobic sulfonated “heads” form the outer ring of the channel with the hydrophilic fluorocarbon “tails” inside of the electron transport channels. To the right, the fluorocarbon tails face outwards, creating a proton channel within the ring.

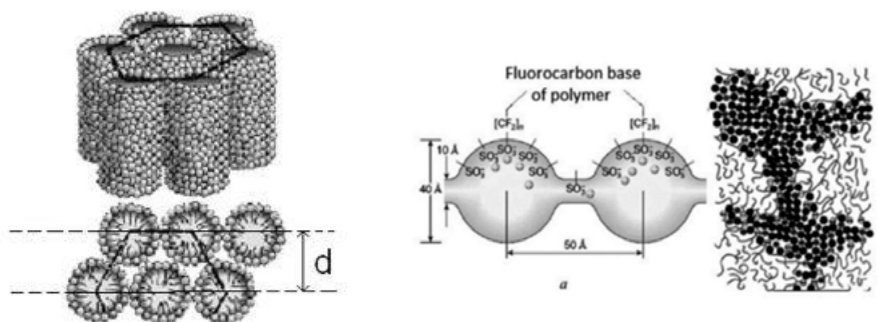


Fig. 5. (Left) Packing structure of PFSA channels; (Right) Microphase separation and channels in PFSA

2.4. Composite Membranes

High Performance Ionomers for water transport require water adsorption in order to function. However, water channels in the Ionomer make the polymer structure weak (gel like). High water content increases the water transmission rate but decreases the mechanical strength. The ideal membrane system is thin (shortest transport path), strong (durable and easily installed), and utilizes highest functionality polymer (i.e. highest water adsorption). In order to address the competing requirements of high-water transmission (i.e. thinness) and mechanical strength, membranes are typically made by reinforcing the functional polymer with a mechanically strong structural element – i.e. composited.

Therefore, composite membranes consist of at least two structural elements made from different materials, as shown in Figure 2. A single-layer composite membrane consists of a thin, selective layer atop a microporous support. The support provides mechanical strength, whereas the water transmission is performed by the thin top-layer. A multi-layer composite membrane can consist of a porous support and many layers of different materials, each performing a specific function. Thin-film composite membranes are typical for pervaporation applications.

The selective layer can be applied by lamination, solution coating, interfacial polymerization, or plasma polymerization methods. Compared to integrally-skinned asymmetric membranes, composite membranes offer several significant advantages: (i) independent selection of materials from which the separating layer and the porous support are formed, (ii) independent preparation of the separating layer and the porous support membrane, thereby making it possible to optimize each structural element, and (iii) very expensive membrane materials (>1000 \$/lb) can be used because only a very small amount of polymer is required for the formation of the thin separation layer (~ 1 g polymer/m² of membrane for a 1- μ m-thick selective layer).

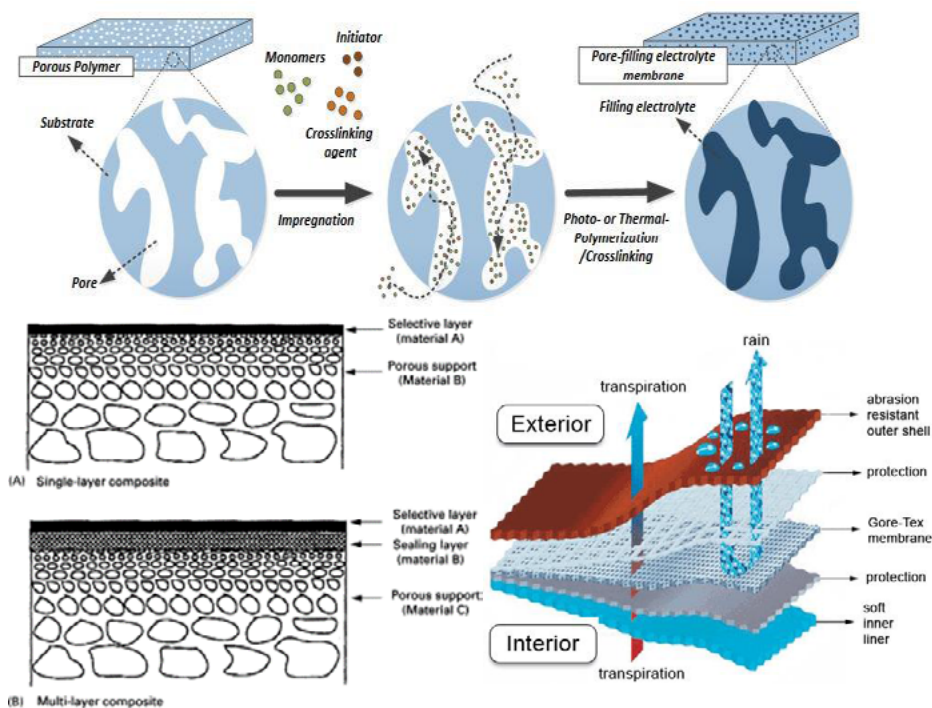


Figure 6: (Top & bottom left) Graphics showing functional polymer combined with porous reinforcement to form a reinforced non-porous composite membrane; (bottom right) composite structures in clothing industry

Composite structures are very common in the clothing industry. Beyond ionic polymers, other polymers that provide water transmission can be found in fabric underwear. For example, the simplest sort of rain wear is a two-layer sandwich. The outer layer is typically nylon or polyester and provides strength. The inner one is polyurethane (PU), and provides water resistance, at the cost of breathability. Polyether Block Amide are also now increasingly used for footwear applications. This schematic (Figure 6, bottom) describes a composite structure developed by W.L. Gore and Associates for the fabrics industry.

3. Experiment & Results

3.1. Description of Test Conditions

Reinforced and unreinforced membranes were tested using a modified method based on ASTM E96 standards developed to determine the moisture vapor transmission rate (MVTR) of highly permeable materials [12]. The test consists of a cup filled with saturated NaCl solution and sealed with ePTFE (expanded Polytetrafluoroethylene). A layer of ePTFE is attached to a support and set to float in a freshwater bath. The membrane to be tested is placed on the ePTFE film and the saltwater cup is inverted on it. The saturated NaCl solution in the cup acts as a desiccant and provides a driving force for the movement of water from the tub to the cup. The cup is weighed after 10 minutes and the increase in weight represents water transport through the

membrane. The average moisture vapor transfer rate was calculated from this weight change and was then normalized by the area of the membrane and the pressure differential across the membrane. The room and bath temperatures were controlled at 20°C. The saturated NaCl solution provides a RH of 75%. At 20°C, the saturation vapor pressure is 2.33 kPa and the pressure differential, the driving force of the mass transfer, is 0.5825 kPa.

Table 1. Different reinforcements and their properties

Support	Construction	Thickness (μm)	Porosity
R1	ePE	5	60%
R2	ePTFE	3	80%
R3	ePTFE	10	80%

As seen in Table 1, two different reinforcement constructions were investigated: expanded polyethylene (ePE) and expanded polytetrafluorethylene (ePTFE). The expanded polytetrafluorethylene support was tested at two different thicknesses. As seen in Table 2, these reinforcements were coupled with three different ionomers to make a reinforced membrane: two cationic ionomers, a long perfluorosulfonic acid (PFSA) (ionomer A) and a garment membrane (ionomer B); and an anion exchange ionomer (ionomer C). In addition to reinforced ionomers, unreinforced membranes were made using ionomers B and C.

Table 2. Membrane permeabilities

MVTR Test Index	Ionomer	Reinforcement	Thickness (μm)	Permeance ($\text{g}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$)
1	A	R3	25	2.51×10^5
2	B	R1	10	4.67×10^5
3	C	R2	5	2.15×10^5
4	B	-	25	6.90×10^5
5	C	-	15	6.82×10^5

3.2. Results & Analysis

As seen in Figure 7, membranes without reinforcement outperformed membranes with reinforcement, due to the increased channel distance and the hydrophobicity of the reinforcement. Of the unreinforced membranes, the garment membrane shows the greatest potential for further research. It outperformed the PFSA and AEM, despite being a thicker membrane. The potential of the water vapor transmission of ionomer B becomes even more apparent when the permeance was normalized to the thickness (Figure 7b). While these unreinforced membranes had sufficient mechanical strength for the 0.5824 kPa driving pressure differential, in an HVAC application the driving pressure can easily exceed 5 kPa, and even 100 kPa, depending on the design of the system. These high pressures will increase the crossover and possibly even burst the unreinforced membrane. Furthermore, because the unreinforced membranes gain their mechanical stability from their thickness, they tend to be significantly more expensive, requiring more ionomer resin than a reinforced membrane.

Of the reinforced membranes, sample 2, the garment membrane supported by ePE, performed the best. This is particularly significant as ePE was not the thinnest membrane and exhibited the lowest porosity, both key factors in water transport through porous membranes. However, by imbibing the material with garment ionomer, the material outperforms thinner membranes with higher porosity.

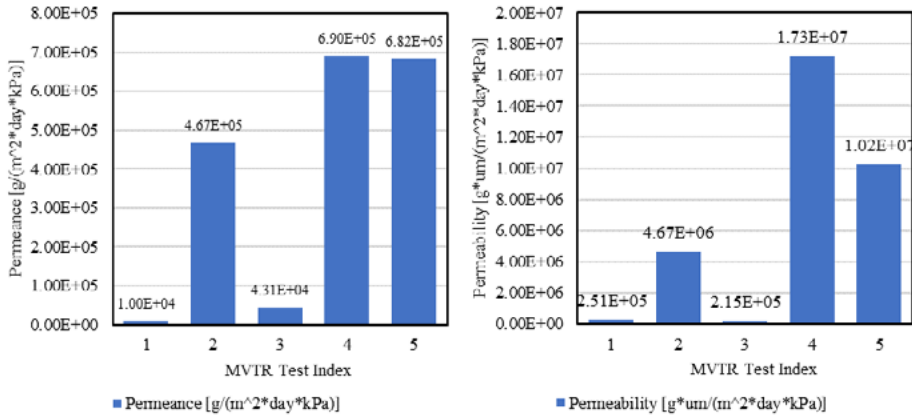


Fig. 7. Comparison of permeance of different membranes (left) and comparison of permeability (permeance normalized to membrane thickness) (right)

Conclusions

The HVAC industry has been relatively slow to adopt the use of water transmission membranes for its applications. Until relatively recently, most ERV modules for example, used paper media as the interfacial layer between incoming and outgoing air streams. In ILD systems, porous structures that allow for bulk flow across them are also very common.

These results confirm that thinner non-porous membrane layer does exhibit the highest water permeation rate – consistent with theoretical expectations. While transmission rates (normalized for thickness) are generally lower in the ‘bulk polymers’ compared to porous membranes, by reducing the thickness of the polymer layer you can more than compensate for the rate reduction, and obtain water transmission rates (permeability) that are comparable – or indeed better than porous membranes. While at the same time, also take advantage of the greater selectivity (i.e. reduction in cross stream contamination). This remains true for both polymers and all supports. Also, crucially, the thinnest (highest performance) membrane is also the lowest cost system.

This outcome is disruptive and transformational, because it enables entry into many historically ‘cost’ sensitive applications – where impervious membranes have always been an attractive but also prohibitively expensive engineering option.

To move this membrane technology to the market, larger scale application testing must be performed. In the theoretical application to a subtropical monsoon climate similar to that of New Delhi, the average daily latent cooling load of a 90 m² apartment is about 2.67x10⁴ kJ or about 11 kg of water per day. Assuming the same pressure drop through the air conditioner would provide a similar driving pressure as in the MVTR testing (0.5825 kPa), the air conditioner would require about 4 m² of the best performing reinforced membrane or about 2.8 m² of the unreinforced membrane. Further research into the design of such a system can be made to determine and improve the driving pressure differential. This research would also help to determine the coefficient of performance of the system – which is directly related to the fan speed and driving pressure differential.

This is especially true for reinforced (composite) membranes since very thin non-reinforced membranes are simply too weak for engineering integration. Typically, a decrease in thickness corresponds to a decrease in mechanical properties. By combining a reinforcement with the functional polymer, a new class of high-water transmission membrane is now available to the HVAC industry.

4. Nomenclature

Table 2. Acronyms and abbreviations, defined

Term	Definition	Term	Definition
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ePE	Expanded polyethylene	PFSA	Perfluorosulfonic acid
ePTFE	Expanded polytetrafluoroethylene	PI	Polyimides
ERV	Energy recovery ventilator	PSSA	Polystyrenesulfonic acid
HVAC	Heating, ventilation and air conditioning	PU	Polyurethanes
ILD	Ionic liquid desiccant	PVA	Polyvinyl alcohol
ILHP	Ionic liquid desiccant	S-SEBS	Sulfonated styrene/ethylene-butylene/styrene
MVTR	Moisture vapor transmission	WBE	Water-based evaporator
PAN	Polyacrylonitrile		

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