# A review on humidification membrane materials for fuel cells

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# Abstract

Polymer electrolyte membrane (PEM) fuel cells have the potential to replace fossil fuel sources in both automotive and auxiliary stationary power generation applications. Increased implementation of fuel cells would decrease dependence on oil and reduce greenhouse gas emissions. However, a major obstacle preventing widespread adoption of fuel cells is cost. The two largest contributors to fuel cell costs are platinum catalyst loading and fuel cell power density. The general strategy for increasing power density and decreasing costly catalyst loading remains unchanged regardless of the catalyst used, i.e., to run the fuel cell at higher temperatures and pressures. Present-day automotive fuel cells typically operate over a temperature range of 50-90°C and pressures up to 3 atm. Increasing temperature and pressure allows for reduced catalyst loading and higher voltage output from the fuel cell. These harsher operating conditions require new membrane materials for thermal and water management. This review provides a summary of a variety of humidification membrane materials, both existing and under development, in order to identify a humidification membrane material capable of operating at higher temperature and pressure conditions to increase fuel cell efficiency and lower the humidification. Copyright © 2018 VBRI Press.

Keywords: Fuel cell, humidification membrane, high temperature membrane.

# Introduction

Polymer electrolyte membrane (PEM) fuel cells have the potential to replace fossil fuel sources in both automotive and stationary power generation applications. Increased implementation of fuel cells would decrease dependence on oil and reduce greenhouse gas emissions. One major obstacle preventing widespread adoption of fuel cells is cost. The Department of Energy (DOE) has set a target cost of \$30/kW for automotive fuel cells to reach in order to be competitive with competing technologies in the projected automotive market. The latest cost analysis report commissioned by the DOE prices systems at \$55/kW for a production rate of 500,000 systems per year, nearly twice the target value [1]. Major improvements must be made rapidly to meet the DOE's goal.

PEM fuel cells convert hydrogen into electric energy, producing water and heat that exit the system as waste products. The reaction can be expressed as

$$2H_2 + O_2 \leftrightarrow 2H_2O \tag{1}$$

Fig. 1 illustrates the operation of a PEM fuel. Pressurized hydrogen gas is supplied to the anode side of the fuel cell, which has channels to direct the gas evenly to a platinum catalyst. The catalyst speeds up the separation of hydrogen gas into H+ ions and electrons. The H+ ions pass through the electrolyte membrane to the

cathode. The electrons cannot pass through the electrolyte membrane and are directed through a circuit as usable electricity. The electrons and H+ ions meet with incoming air in the cathode, which supplies oxygen to form water in the presence of another platinum catalyst layer.



Fig. 1. Schematic of a PEM fuel cell.

The two largest contributors to fuel cell costs are platinum catalyst loading and fuel cell power density [1]. Market fluctuations in platinum prices have held estimated fuel cell prices constant over the past few years despite improvements in fuel cell systems and materials. There is a major research focus on developing new catalysts to reduce cost by creating composite catalysts with reduced platinum loading or nanostructured catalysts with no platinum at all [2-4]. These new catalysts may decouple fuel cell prices from platinum fluctuations. The general strategy for increasing power density and decreasing costly catalyst loading remains unchanged regardless of the catalyst used, i.e., to run the fuel cell at higher temperatures and pressures. Present-day automotive fuel cells typically operate over a temperature range of 50-90°C and pressures up to 3 atm. The Nernst Equation demonstrates cell voltage has a linear dependence on temperature and a logarithmic dependence on pressure, assuming the concentration ratio of reactants is held constant:

$$\Delta V = \frac{RT}{2F} \ln \frac{\alpha \beta^{1/2}}{\delta} P^{1/2}$$
(2)

where R is the universal gas constant, T is temperature, F is Faraday constant, P is system pressure and  $\alpha$ ,  $\beta$ , and  $\delta$  are constants that represent the concentration of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O, respectively [5].

Increasing temperature and pressure allows for reduced catalyst loading and higher voltage output from the fuel cell. These harsher operating conditions require new thermal and water management solutions. Currently, fuel cell humidification costs generally make up less than 15% of total system cost [1, 6]. However, a fuel cell system analysis conducted by Argonne National Labs estimated a ten-fold increase in membrane humidifier surface area was needed when the exit temperature at the cathode was raised from  $85^{\circ}$ C to  $95^{\circ}$ C [4]. Humidification costs may further increase as the DOE has targeted temperature values of  $120^{\circ}$ C for automotive applications and  $150^{\circ}$ C for stationary applications [1, 7].

Careful control of relative humidity levels within the electrolyte membrane is required for both efficiency and Currently available reliability [8,9]. electrolyte membranes require humid conditions to function; if humidity levels are too low, membrane conductivity and power output are reduced. Higher than optimal humidity levels cause excess water to flood the PEM, blocking gas flow and reducing output [10]. There are a variety of options for fuel cell humidification; however, membrane humidifiers either external or internal to the fuel cell are currently the most promising solution [11]. They are the only system that can recycle waste heat and humidity passively with no moving parts.

Nafion was developed by DuPont in the 1960's to process chlorine and caustic soda [12]. It has been the membrane material of choice for PEM fuel cell humidifiers due to its excellent water and ion transport characteristics. However, its ion transport properties are not necessary for humidification and its high price ( $\sim$ \$1000/m<sup>2</sup>) drives up the cost of the entire fuel cell system. Nafion has a maximum operating temperature of  $\sim$ 100°C, after which it becomes difficult to maintain membrane moisture content [13]. Even if moisture content is maintained, the material begins to decompose at 110°C due to the glass transition temperature of its PTFE support structure [13]. Furthermore, anhydride formation occurs due to oxidation under normal fuel cell operating conditions an can result in performance decreases of up to 70% [7].

There are a variety of humidification membrane materials under investigation, but none have satisfied the requirements outlined by the DOE. Developing a less expensive humidification membrane capable of operating at the new conditions outlined by the DOE is necessary to increasing fuel cell efficiency and lower humidification costs. This review provides a summary of various humidification membrane materials, focusing on higher temperature and pressure capabilities. We start with a discussion on material development strategies and then review the characteristics of major material systems, including both established and under development.

#### Material development strategies

Membranes can generally be classified as homogenous, composite, asymmetric, ion exchange, microporous, or some combination of these, as seen in **Fig. 2** [14]. For humidification membranes, the primary performance metric is the water permeation rate, but maximizing operational temperature and minimizing cost are also important. Materials must also have a low air permeation rate, high oxidative resistance and sufficient mechanical strength to withstand pressure differences and RH/temperature cycling [15]. Various strategies could be used to improve the membrane performance. **Table 1** summarizes the key benefits and disadvantages of each of these membrane development approaches.

Symmetrical membranes



Fig.2. Diagram of membrane types [16].

One of the most common strategies used to increase water permeation rate through materials is reducing cross sectional thickness. According to Darcy's law liquid mass flow rate, Q, through a membrane is governed by

$$Q = \frac{-kA(p_b - p_a)}{\mu L} \tag{3}$$

where k is intrinsic permeability, A is cross sectional area,  $\Delta p$  is pressure drop,  $\mu$  is viscosity of the fluid, and L is thickness. The simplest way to increase Q is to make the membrane as thin as possible. This approach is applicable to all membrane types, however reducing thickness comes include the cost of decreased mechanical stability [17]. [20]

 Table 1. Summary of membrane development approaches.

Strategy	Pros	Cons
Reduce	<ul> <li>Increased</li> </ul>	<ul> <li>Reduction in</li> </ul>
thickness	permeability	tensile strength
Anisotropic composite	<ul> <li>Retains permeability of thin active layer</li> <li>Increased strength from support layer</li> </ul>	<ul> <li>CTE mismatch can induce stress and cause delamination</li> <li>Swelling can induce stress and cause delamination</li> </ul>
Mixed matrix membrane	<ul> <li>Higher strength</li> <li>Simple fabrication</li> <li>Filler can increase permeability and selectivity</li> <li>Can be melt processed</li> </ul>	<ul> <li>Lower permeability than thin film anisotropic</li> <li>Difficult to achieve uniform dispersion</li> <li>Polymer-filler interaction can be difficult to achieve</li> </ul>
Multiblock polymers	<ul> <li>Potentially improved properties</li> </ul>	<ul> <li>Unpredictable properties</li> <li>Time consuming to develop</li> </ul>
Sulfonation	<ul><li>High water permeability</li><li>Highly selective</li></ul>	<ul> <li>Limited operating temperature</li> <li>Anhydride formation concerns</li> <li>Increased swelling can cause stress and rupture</li> </ul>

One approach to improving the strength of thin membrane is to create a thin-film composite anisotropic membrane by fixing a thin selective membrane to a porous support structure. The support structure provides mechanical strength and the thin membrane remains highly permeable [16]. This approach requires careful design to avoid delamination. Membrane separation could occur as a result of stresses induced by thermal cycling due to a coefficient of thermal expansion (CTE) mismatch between the active membrane and support structure. Relative humidity cycling also causes delamination due to induced mechanical stress from membrane swelling [15]. The support structure can be polymer or inorganic, with inorganic ceramic supports often employed in desalination. One method of making these composites is to dip coat the porous support structure in a polymersolvent solution. Depending on the wetting characteristics of the support structure and solution, the polymer and solvent may penetrate too far into the support structure. This can be mitigated by pre-wetting the support with water [18].

Composite materials can also be created by adding particles to a polymer to create a mixed matrix membrane (MMM) [16, 19]. Researchers have attempted to enhance membrane properties with many inorganic additives including silica, zeolite, titania and carbon nanotubes [20]. These particles interact with the surrounding polymer and have been shown to enhance separation factor, polymer free volume, and ion transport characteristics. In order to be effective, the fillers must be well distributed within the polymer; often additives will prefer to aggregate rather than bond to the polymer and require surface functionalization to disperse [20]. Amphiphilic surfactants can be useful in this regard, as they have both hydrophilic and hydrophobic properties that allow them to bond to the base polymer and additive [20].

Another strategy to meet both water permeation and strength requirements is to blend hydrophobic and hydrophilic polymers. Hydrophobic polymers generally have high crystallinity and therefore superior mechanical properties compared to hydrophilic polymers at increased temperature [15]. Hydrophilic polymers have superior water transport characteristics. Combining the two can result in a permeable polymer capable of operating at higher temperatures. Schult et al. blended hydrophobic polysulfone (PSF) with hydrophilic water-soluble poly (vinyl pyrrolidone) (PVP) to enhance water sorption and permeability [21]. Weight loading had to be limited to 40% PVP as greater loadings caused phase separation and loss of PVP by liquid water. Similar results were achieved by mixing polyethersulfone (PES) with up to 20% polyethyloxazoline (PEOX) [22].

The water permeation rate and selectivity can also be increased by adding sulfonic, carboxylic, or phosphoric acid sites to make polymers more hydrophilic [20, 23]. The most common process is sulfonation, which replaces a hydrogen atom on an arene with a sulfonic acid group, as seen in Fig. 3. This can be accomplished either through copolymerization of a sulfonated and non-sulfonated polymer through polymer sulfonation. or Copolymerization offers better control of sulfonation and can create ordered water channels between hydrophobic and hydrophilic domains [20]. The placement of sulfonic acid sites during sulfonation is dependent on the method used as well as the polymer structure [20]. The degree of sulfonation can be controlled by the agent concentration, exposure time and reaction temperature [20]. In addition to water transport enhancement, sulfonation also gives a polymer desirable ion transport characteristics, as it allows protons to move between ion groups across the membrane without conducting electrons.



Fig. 3. Illustration of a sulfonation reaction [24].

Sulfonated materials however often suffer mechanical failures due to the stress induced by relative humidity cycling. This stress may be induced by material swelling due to movement of sulfonated ion groups during water transport. Swelling can be reduced by increasing polymer free volume or crosslinking, but crosslinking increases brittleness [20]. Some polymers do not respond well to sulfonation, and lose mechanical strength or become water soluble [23]. The possibility of desulfonation also limits operational temperature. Increasing polymer free volume also tends to increase water permeation rate [21].

## Established material

Commercially available Nafion has excellent water and ion transport characteristics that have made it the most commonly used material in fuel cells [25]. Nafion is classified as sulfonated tetrafluoroethylene, consisting of a hydrophobic PTFE structure supporting sulfonated ion side chains [26]. This combination of hydrophobic backbone and hydrophilic side chains results in highly ordered water transport channels that reduce swelling and increase water transport [20]. It is initially hydrophobic



Fig. 5. Nafion cluster network model [28].

These Nafion composites show improved performance in some areas but generally have reduced water transport characteristics and proton conductivity because the composites contain fewer sulfonated groups [13]. A new material is required to improve maximum fuel cell operational temperature and overall reliability.



Fig. 4. Nafion swelling in response to water exposure [26].

when dry but becomes hydrophilic as water contact draws sulfonic acid domains to the material surface, as seen in **Fig. 4** [26]. Sulfonic acid domains provide the means of water transport through Nafion, and as they move to take on water Nafion swells. As a result there is no convective water flow across the membrane [25].

The exact structure of Nafion is a topic of debate because it is very difficult to image. Part of the difficulty in imaging Nafion arises from the fact that its structures span multiple size domains; Small-angle X-ray scattering (SAXS) has shown a distance of ~5 nm between hydrophilic domains, while the crystalline Teflon backbone is much larger [25]. Further complicating matters are the conformational changes the structures undergo when exposed to water as Nafion swells. One of the proposed Nafion structural models, the cluster network model, can be seen in Fig. 5. Despite the presence of well-ordered water channels, there is still a large shift in domain size and subsequent swelling when Nafion is exposed to water. Alternating hydrated and dehydrated states result in significant mechanical stress from relative humidity cycling during fuel cell operation. A standard DOE mechanical stress test demonstrated Nafion failure after ~3500 humidity cycles [27]. Researchers have developed a variety of inorganic Nafion composites to increase maximum operation temperature [28].

## Materials in development

## Gore M311

W. L. Gore & Associates is developing a high water flux membrane to be used in fuel cell humidification applications. They have combined an unspecified 5 micron thick PFSA ionomer membrane with ePTFE backing layers for support. The material is very thin to increase water flux rates, but needs to be supported due to lack of mechanical strength, making this a thin-film composite anisotropic membrane. According to James et al., the steps most likely used to create the thin ionomer membrane structure are to unroll ePTFE layer on Mylar® backer, die-slot coat layer of ionomer onto ePTFE, unroll second ePTFE layer onto ionomer, pass through continuous curing oven, laminate with PET layer, and wind onto roll [29].

Initially, Gore experimented with coating the ionomer on ePTFE then Mylar. Eventually they settled on a sandwich structure, seen in **Fig. 6**. A diagram of the final structure can be seen below in **Fig. 7**.

Gore has been able to achieve high flow rates with M311, but available information is limited because the material is proprietary and currently in development. Objective initial testing shows the material suffers from degradation at temperatures above 80°C due to ionic species contamination and formation of sulfonic

anhydride [31]. A lower operating temperature than Nafion is undesirable when fuel cells will need increased operating temperatures to increase efficiency.



Fig. 6. Ionomer on microporous substrates, seen in (a) and sandwich form seen in (b). The 5 micron ionomer layer is more clearly seen in (c) and (d) [30].



Fig. 7. Diagram of composite membrane [29]

#### "PFCB" material

Tetramer is working in conjunction with the DOE to develop new humidification membrane materials. Their approach is to use something they call "PFCB polymer technology" to combine different functional groups and synthesize new polymers capable of meeting the demands placed on humidification membranes. They categorized these demands into four groups: water permeability, mechanical strength, stability and processing. Their approach to meeting each of these needs can be seen in **Fig. 8**.



Fig. 8. Tetramer approach to synthesizing new humidification membranes [7].

As a result they have synthesized 15 new monomers and 26 new polymers with the goal of providing multiple water transport pathways and reduced degradation [7]. The best result achieved is testing for 240 hours at 80°C, 95°C and 4 hours at 140°C with no anhydride formation detected. Water permeation testing produced a value of 2.58g/m<sup>2</sup>\*s, although little information was given about testing conditions. However, like the Gore membrane the Tetramer membrane cannot operate above 100°C over extended periods of time. Like Nafion, mechanical stress cycling due to relative humidity changes generated leaks and the material no longer functioned as a barrier to gas. Their initial analysis indicates the residual solvent (dimethlyacetamide) is to blame and are exploring other solvent options.

#### Wicking materials

A stainless steel passive wicking humidifier was proposed for use in fuel cell applications by TeGrotenhuis et al [32]. The design uses Pall Supramesh, a material made from stainless steel powder sintered to stainless steel woven wire mesh, as a humidification membrane. The main water transport mechanism is capillary action, which drives water from the humid cathode exhaust to evaporate in the dry inlet air stream. The use of stainless steel in a thin film for humidification is counter-intuitive, but it can withstand high temperatures and is resistant to thermal and humidity cycling. Tensile test samples showed no significant change in strength after freeze/thaw cycling at 95% RH for 28 days (MIL-STD-331C) [32].

Wicking humidifiers rely on the bubble point pressure to prevent air crossover between the dry and humid air streams. When porous structures and meshes are fully wetted, the capillary forces between the structure and water oppose gas flow, which can be quantified as a bubble point pressure. Capillary performance in wicks is dependent on both the effective pore radius and contact angle within the wick [33]. The effective pore radius of a mesh can be calculated by a bubble point test, where pressure difference across a wetted sample is increased until a continuous stream of bubbles forms on the other side. Effective pore radius  $r_c$  is given by

$$r_c = \frac{2\sigma\cos\theta}{\Delta P_c} \tag{4}$$

where  $\sigma$  is surface tension in N/m,  $\theta$  is contact angle, and  $\Delta P_c$  is capillary pressure difference in Pa. Contact angle between the mesh and fluid is measured with an optical microscope [33].

Although the Supramesh material showed promise, alternatives were sought to reduce cost and increase performance. Direct powder rolling of 430 stainless steel was explored as an alternative. Initial testing showed powder rolling could produce a material with twice the bubble point pressure of Supramesh and similar water permeability. The microstructure of the powder rolled 430 SS can be seen in **Fig. 9**, produced with a thickness of .03 to .05 inches [32].



Fig. 9. 430 SS wick structure [32].

One of the main downsides to this material is the high cost of stainless steel. Material prices were estimated at \$110 per device alone, driving the total humidifier cost to nearly \$170. The other main drawback is that, like Nafion, the device must be wet to function as a barrier. This means significant start up time (30 minutes during testing) before optimal operation can be achieved. However, the startup time could be mitigated if the humidifier is not allowed to dry out. The 80 kW mesh humidifier was projected to weigh less than 9 kg, which is less than an enthalpy wheel but above the DOE target of 5 kg [34]. While the design was not feasible, the concept of using the bubble point may be applicable to future materials.

#### **Polyamides**

Polyamides are dense, nonporous membranes usually used for gas separation up to temperatures of ~70°C [14]. They are susceptible to oxidation and surface fouling which make them unsuitable for use as a fuel cell humidification membrane [14]. They are commonly used for water desalination, where the highest water flux polyamides available can achieve flow rates of ~10 g/m<sup>2</sup>\*s but require a pressure differences of 250 psi [35]. The operational temperature range is also quite low for polyamide reverse osmosis membranes. FILMTEC-30, available from Dow chemical, is a thin aromatic polyamide membrane supported by a porous polysulfone layer with a maximum operating temperature of  $45^{\circ}$ C [36].

#### **Polyimides**

UBE Industries offers a polyimide membrane designed for dehydration of solvent-water mixtures with an operating temperature of up to 120°C, but it requires a vacuum on the permeate side [37]. There is no mention of water transfer rate. Sulfonated polyimide has been investigated for use in direct methanol fuel cells (DMFC).

#### Polydimethylsiloxane (PDMS)

PDMS or silicone is a gas permeable, dense, polymeric membrane with high water permeability despite its hydrophobicity [18]. As a result, PDMS composites are often used for separation of ethanol/water mixtures in pervaporation. Permselect offers fuel cell humidifiers with hollow silicone fibers, similar in principle to the Perma-Pure Nafion humidifier. However, the system requires an external water supply and is not available for gas-gas humidification, indicating its water vapor transfer rate is too low.

#### Sulfonated hydrocarbons

Various non-fluorinated sulfonated polymers have been developed as an environmentally friendly replacement for Nafion in PEM fuel cells. These polymers tend to have more swelling when hydrated and lower chemical resistance than Nafion [20]. Sulfonated poly(ether ether ketone) (sPEEK) has a higher water content, lower gas crossover and more hydrophilic domains than Nafion, yet has only demonstrated water flux rates about ~50% of those recorded in Nafion for similar material thickness [38]. Water flux for Nafion and sPEEK can be seen in **Fig. 10**. The difference in water flux between the two materials demonstrates that organization of sulfonated domains is an important consideration, not just the total level of sulfonation. Furthermore, sPEEK tends to swell and dissolve under high temperature and relative humidity [38]. For these reasons, sPEEK tends to be used in direct methanol fuel cells.



Fig. 10. Liquid-vapor permeation of Nafion and sPEEK membranes [38]

Nexar is a sulfonated pentablock styrene based copolymer membrane from Kraton [23, 39]. There is limited information available, but it appears to be a promising desalination membrane. However, water permeation rate data is only available up to  $55^{\circ}$ C, with a maximum rate of ~.8 g/m<sup>2</sup>s for the MD9150 variant and ~1.1 8g/m<sup>2</sup>s for the MD9200 variant [39]. These flux rates are less than half those achieved in Nafion, although the maximum operating temperature is unclear. Lower water permeability could be acceptable if it comes with higher maximum operating temperatures.

#### **Zeolite composites**

Zeolite composites are a promising humidification membrane material, currently being researched primarily for desalination applications [40-52]. Zeolite is a naturally occurring. microporous aluminasilicate material, generally available in particulate form. Fig. 11 shows a scanning electron microscope (SEM) image of zeolite particles, uniform in morphology and size. Zeolite is both highly permeable and selectively permeable; it has uniformly sized pores that do not allow larger sized molecules to pass through, separating them from smaller molecules [19, 40]. Zeolite pore size varies with species, making it an ideal material for use in gas/gas or liquid/gas separation [52].



Fig. 11. SEM image of zeolite particles [42].

Zeolites are also mechanically and thermally stable above 500°C, which makes them suited to a fuel cell operational environment [18, 19, 41]. Since zeolite is quite brittle, it is generally deposited on a support structure to create a composite membrane or used as an additive in melt processing to create a symmetric membrane [18, 40]. Composite membranes usually achieve higher fluxes than symmetric membranes in pervaporation [18]. However, the composite membranes are usually zeolite deposited onto a hollow ceramic support [18]. These composites are generally developed for desalination and water purification in order to lower the pressure difference and energy required to separate water from a given contaminant [44]. Zeolite has been combined with a variety of polymers including PDMS, EPDM, and PVA.

Zeolite can also be added to polymers to create a MMM. Gongping et al. combined zeolite with PDMS for pervaporation applications [18]. Zeolite deposited into a hydrophobic material may aggregate instead of interacting with the polymer. Gongping et al. grafted zeolite with n-octyl chains using ocyltriethoxysilane to increase polymer-filler interaction. Zeolite has also been added to a porous polysulfone support structure for desalination [43]. The addition of zeolite into polymers can enhance gas separation properties and improve membrane water retention [14, 16].

Direct comparison between Nafion and zeolite water flux rates is difficult due to the large number of Nafion and zeolite varieties as well as the differences in experimental setups and test conditions. Zhou *et al.* reported a flux rate of up to  $3.37 \ kg/m^2h$  of pure water through a thin zeolite membrane deposited on a support layer [41, 51]. Data from Shao et al. shows flux rates between 9 and 11  $kg/m^2h$  for zeolite membranes, although this was for an ethanol solution at 75°C [48]. Data from Adachi et al. reported flow rates between 3 and 9  $kg/m^2h$  for Nafion NRE211 at 70°C, making the zeolite membranes competitive [53]. The flow rate of zeolite composites is often limited by the support structure, not the zeolite. A highly porous support structure could meet or exceed Nafion permeability [48].



Fig. 11. Solid-state foamed PES-Zeolite composites: (a) Cross sectional SEM image of foamed PES-Zeolite membrane, (b) comparison of membrane water vapor transfer rate [54].

## Foamed PES-Zeolite composites

The MMM approach involves combining a polymer matrix with an inorganic filler material to improve selectivity and permeability. This approach has the advantage of embedding the active selection layer within the polymer to protect it from delamination. However, the main drawback of MMM is generally reduced permeability when compared to sulfonated materials. To overcome this problem, a solid state foaming process has been employed to create a foamed PES-zeolite MMM, where the foaming process effectively embeds the porous support structure within the membrane to increase water permeability[54,55]. Polyethersulfone (PES) has excellent thermal and mechanical properties, including a glass transition temperature of 220 °C. With PES as the matrix material, the fabricated membrane satisfies the high temperature requirements for fuel cell humidification membranes. Fig. 11 shows a cross sectional SEM image and water vapor transfer performance of a foamed EPSzeolite composite [54]. As shown in Fig. 11(a), the zeolite appears to act as a nucleation agent for pore formation since some of the visible pores contain zeolite particles. The PES matrix appears to have interconnected pores. The foamed film appears to be permeable, whereas before foaming there were large material sections with low zeolite loading and no pores to create a path for water transport. The effect of foaming on permeability is shown in **Fig. 7(b)**. Unfoamed samples, even with zeolite composites, had a water permeation performance similar to virgin PES membrane. On the other hand, foamed samples had much higher permeation performance, close to that of Nafion.

#### **Conclusion and future perspectives**

Target fuel cell system specifications from industry and DOE clearly established requirements for new humidification solutions. High temperature stability and ability to withstand repeated changes in relative humidity were determined to be the most important membrane properties. Passive humidity recycling systems are the most likely to be employed for future use due to simplicity, low cost and efficiency. A variety of established materials and materials in development were examined with respect to their strengths and weaknesses for suitability for high-temperature operations. There is a gap between existing membrane materials and the high temperature requirement of automotive fuel cell humidifiers. For future development, thin cross section and mixed matrix membranes were determined to be a promising approach as they offer increased water flux and selectivity while avoiding swelling and temperature limits imposed on thin film composites and sulfonated materials.

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#### References

- James, B.D.; Moton, J.M.; Colella, W.G., Fuel Cell Transportation Cost Analysis, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2014 Annual Merit Review and Peer Evaluation Meeting 2014: Washington, DC.
- 2. Hsieh, Y.-C.; Zhang, Y.; Su, D.; Volkov, V.; Si, R.; Wu, L., et al.; Nature communications, 2013. 4.
- 3. Cheon, J.Y.; Kim, T.; Choi, Y.; Jeong, H.Y.; Kim, M.G.; Sa, Y.J., et al.; Scientific reports, **2013**. 3.
- 4. Ahluwalia, R.K.; Wang, X., Fuel Cells Systems Analysis, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Merit Review and Peer Evaluation Meeting 2014: Washington, D.C.
- Rayment, C.; Sherwin, S., Introduction to fuel cell technology. Dept. Aerospace & Mechanical Engineering, Notre Dame, 2003.
- Satyapal, S.; Mills, M.; Byham, S.; Hou, Z.; Nahm, K.S., Fuel Cell Cost Analysis Summary, 2008, IPHE.
- Wagener, E.H.; Morgan, B.P., New High Performance Water Vapor Membranes To Improve Fuel Cell Balance of Plant Efficiency and Lower Costs, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2014 Annual Merit Review and Peer Evaluation Meeting 2014: Washington, D.C.
- Headley, A.J.; Chen, D.; Li, W.; International Journal of Hydrogen Energy, 2017. 42(36) 23170-23179.
- 9. Chen, D.; Li, W.; Peng, H.; Journal of Power Sources, 2008. 180(1) 461-467.
- Chen, D.; Peng, H.; Journal of Dynamic Systems, Measurement, and Control, 2005. 127 424-432.
- 11. Yoshida, T.; Kojima, K.; *The Electrochemical Society Interface*, **2015**. 24(2) 45-49.
- 12. Gates, C.M.; Newman, J.; AIChE Journal, 2000. 46(10) 2076-2085.
- Yang, C.; Srinivasan, S.; Bocarsly, A.; Tulyani, S.; Benziger, J.; Journal of Membrane Science, 2004. 237(1) 145-161.
- 14. Hughes, R.; Industrial membrane separation technology1996: Springer.

- Hamrock, S., New Fluorinated Ionomers and Membranes for PEM Fuel Cells, in Fuel Cell Seminar & Energy Exposition, 2011: Orlando, Florida.
- 16. Baker, R.W.; *Membrane Technology and Applications*. Second ed**2004**: John Wiley & Sons.
- James, B.D.; Spisak, A.B., Mass Production Cost Estimation of Direct H2 PEM Fuel Cell Systems for Transportation Applications: 2012 Update, in report by Strategic Analysis, Inc. for the US Department of Energy, 2012.
- Gongping, L.; Wang, W.; Wanqin, J.; Nanping, X.; Chinese Journal of Chemical Engineering, 2012. 20(1) 62-70.
- Basile, A.; Nunes, S.; Advanced Membrane Science and Technology for Sustainable Energy and Environmental Applications 2011: Elsevier.
- Park, C.H.; Lee, C.H.; Guiver, M.D.; Lee, Y.M.; Progress in Polymer Science, 2011. 36(11) 1443-1498.
- 21. Schult, K.; Paul, D.; Journal of Polymer Science Part B: Polymer Physics, 1996. 34(16) 2805-2817.
- Schult, K.; Paul, D.; Journal of Polymer Science Part B: Polymer Physics, 1997. 35(6) 993-1007.
- 23. Geise, G.; Freeman, B.; Paul, D.; Polymer, 2010. 51(24) 5815-5822.
- 24. March, J.; Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (3rd ed.)1985, New York: Wiley.
- Duan, Q.; Wang, H.; Benziger, J.; Journal of Membrane Science, 2012. 392 88-94.
- Goswami, S.; Klaus, S.; Benziger, J.; Langmuir, 2008. 24(16) 8627-8633.
- 27. Benjamin, T.G., Membrane and MEA Accelerated Stress Test Protocols, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2007 Annual Merit Review and Peer Evaluation Meeting 2007: Arlington, Virginia.
- Sahu, A.; Pitchumani, S.; Sridhar, P.; Shukla, A.; Bulletin of Materials Science, 2009. 32(3) 285-294.
- James, B.D.; Moton, J.M.; Colella, W.G., Fuel Cell Transportation Cost Analysis, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2013 Annual Merit Review and Peer Evaluation Report, 2013: Arlington, Virginia.
- Johnson, W.B.; V.J.1 Materials and Modules for Low-Cost, High-Performance Fuel Cell Humidifiers in U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Merit Review and Peer Evaluation Meeting. 2011. Arlington, Virginia.
- Johnson, W.B., Materials and Modules for Low-Cost, High-Performance Fuel Cell Humidifiers, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2012 Annual Merit Review and Peer Evaluation Meeting, 2012: Arlington, Virginia.
- 32. TeGrotenhuis, W.; Caldwell, D.; Lavender, C.; Roberts, B., Low-Cost Manufacturable Microchannel Systems for Passive PEM Water Management, in U.S. Department of Energy Hydrogen and Fuel Cells Program 2008 Annual Merit Review and Peer Evaluation Meeting, 2008: Washington, D.C.
- 33. de Bock, H.P.J.; Varanasi, K.; Chamarthy, P.; Deng, T.; Kulkarni, A.; Rush, B.M., et al.; Experimental investigation of micro/nano heat pipe wick structures in ASME 2008 International Mechanical Engineering Congress and Exposition. 2008. American Society of Mechanical Engineers.
- 34. TeGrotenhuis, W.; Lavender, C.; V.K.2 Low-Cost Manufacturable Microchannel Systems for Passive PEM Water Management in U.S. Department of Energy Hydrogen and Fuel Cells Program 2008 Annual Merit Review and Peer Evaluation Meeting. 2008. Washington, D.C.
- Norris, I.D.; Morrison, M.C.; Mattes, B.R.; High Flux Polyamide Composite Hollow Fiber Membranes for Reverse Osmosis Applications in MRS Proceedings. 2006. Cambridge Univ Press.
- Chemical, D., FILMTEC Membranes: A Comparison of Cellulose Acetate and FILMTEC FT30 Membranes, Tech Facts, D. Chemical, Editor 2014: Dow Website.
- 37. Inc., U.A. *Dehydration Systems* 2014 [cited 2014 October]; Available from: https://www.ube.com/content.php?pageid=21.
- Zhao, N.; Edwards, D.; Shi, Z.; Holdcroft, S.; ECS Electrochemistry Letters, 2013. 2(3) F22-F24.
- 39. LLC, K.P., *NEXAR Polymers*, in *Kraton Website*, K.P. LLC, Editor 2010.
- 40. Bowen, T.C.; Noble, R.D.; Falconer, J.L.; *Journal of Membrane Science*, **2004**. 245(1) 1-33.

- Bowen, T.C.; Li, S.; Noble, R.D.; Falconer, J.L.; *Journal of Membrane Science*, 2003. 225(1) 165-176.
- 42. Ciobanu, G.; Carja, G.; Ciobanu, O.; *Materials Science and Engineering: C*, **2007**. 27(5) 1138-1140.
- 43. Kim, S.G.; Hyeon, D.H.; Chun, J.H.; Chun, B.-H.; Kim, S.H.; *Journal of Membrane Science*, **2013**. 443 10-18.
- Cho, C.H.; Oh, K.Y.; Kim, S.K.; Yeo, J.G.; Sharma, P.; Journal of Membrane Science, 2011. 371(1) 226-238.
- 45. Li, Y.; Yang, W.; Journal of Membrane Science, **2008**. 316(1) 3-17.
- Lind, M.L.; Ghosh, A.K.; Jawor, A.; Huang, X.; Hou, W.; Yang, Y., et al.; Langmuir, 2009. 25(17) 10139-10145.
- 47. Sandström, L.; Palomino, M.; Hedlund, J.; *Journal of Membrane Science*, **2010**. 354(1) 171-177.
- Shao, J.; Zhan, Z.; Li, J.; Wang, Z.; Li, K.; Yan, Y.; Journal of Membrane Science, 2014. 451 10-17.
- Shu, X.; Wang, X.; Kong, Q.; Gu, X.; Xu, N.; Industrial & Engineering Chemistry Research, 2012. 51(37) 12073-12080.
- Ma, L.; Barker, J.; Zhou, C.; Li, W.; Zhang, J.; Lin, B., et al.; Biomaterials, 2012. 33(17) 4353-4361.
- Zhou, H.; Korelskiy, D.; Leppäjärvi, T.; Grahn, M.; Tanskanen, J.; Hedlund, J.; *Journal of Membrane Science*, **2012**. 399 106-111.
- 52. Tavolaro, A.; Drioli, E.; Advanced materials, 1999. 11(12) 975-996.
- Adachi, M.; Navessin, T.; Xie, Z.; Frisken, B.; Holdcroft, S.; Journal of the Electrochemical Society, 2009. 156(6) B782-B790.
- Borduin, R.; Li, W.; Development of Foamed PES-Zeolite Mixed Matrix Membranes for PEM Fuel Cell Humidification in ASME 2016 11th International Manufacturing Science and Engineering Conference. 2016. Blacksburg, Virginia, USA.
- 55. Borduin, R.; Li, W.; Journal of Manufacturing Science and Engineering, 2016. 139(2) 021004-021004-7.