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The effect of temperature and humidity on the oxygen sorption in Diels–Alder polyphenylenes

Charles W. James, Jr. [a], Chris Cornelius [b], Eva Marand [a,*]

[a] Department of Chemical Engineering, Virginia Polytechnic Institute and State University, 138 Randolph Hall, Blacksburg, VA 24061-0211, USA
[b] Sandia National Laboratories, Albuquerque, NM 87285, USA

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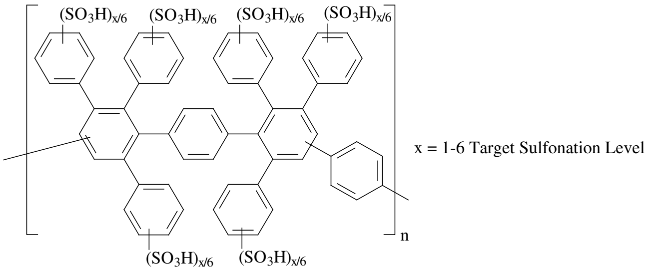
ABSTRACT

The gas transport properties of post-sulfonated Diels–Alder polyphenylene (SDAPP) membranes were measured and compared to poly(perfluoro sulfonic acid) (Nafion 112). The SDAPP materials had ion exchange capacities of 1.6 and 2.2 mequiv/g. The O_2 gas permeability in the SDAPP 2.2 was about half that observed in Nafion@ 112. The O_2 sorption in each membrane was measured in both the non-humidified and humidified state. In the non-humidified state, the O_2 sorption followed Henry's Law behavior. The enthalpy of sorption for the SDAPP materials in the dry state was about double that measured for Nafion@ 112. In the presence of moisture, the O_2 sorption followed Type IV behavior typically exhibited by hydrophilic polymers. The SDAPP samples had a higher percent wet-O_2 mass uptake compared to Nafion@ 112, because of a higher ion exchange capacity.

1. Introduction

In order to overcome cost and performance limitations, numerous research efforts have been aimed at the development of new proton exchange membranes to replace commercially available Nafion@ [1–5]. In principle, alternative materials should have high ionic conductivity, high thermal stability for operation above 100 °C, good chemical stability due to the presence of strong acids used as proton conductors, good barrier properties, and good processibility. One attempt at improving proton exchange membranes consisted of sulfonating existing thermoplastics such as polyketones [4,6,7] and polysulfones [8–10], thus allowing for an increase in thermal stability and a decrease in processing costs. However, these materials have lower ionic conductivities than Nafion@ at the same ion exchange capacity. In addition, these materials have a greater possibility of undergoing acid-catalyzed or oxidative degradation.

A way to overcome these difficulties is to utilize purely aromatic polymers, such as poly(phenylene)s, which have better barrier properties and thermal and chemical stability when compared to Nafion@. Furthermore, the post-sulfonated Diels–Alder poly(phenylene) (SDAPP), structure 1, has shown comparable ionic conductivities to Nafion@ [11].



Earlier studies have shown that proton conductivity and water transport in proton exchange membranes depend on the hydration level of the membrane [12–15]. The extent of hydration depends on the solvation of the acid groups, the amount of additional water bound to the solvated complex and the amount of unbound water within the membrane pore structure. One way to probe the hydration level of the membranes is to measure gas transport. For example, it is expected that the permeability and sorption behavior of small gases will be sensitive to the state of the water present in the membrane system as well as to the molecular structure of the membrane material [12,16]. Since Nafion@ has a different polymer structure, yet comparable conductivity to SDAPP, the transport mechanisms of gases in these two membranes may differ. This gas transport study consists of two parts. In the first part, H_2 and O_2 permeability is measured in the SDAPP membranes containing an ion exchange capacity of 1.6 (SDAPP 1.6) and 2.2 (SDAPP 2.2) mequiv/cm and in Nafion@ 112 to understand the impact of sulfonic acid group content on the transport properties. In the second part O_2 gas

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[*] Corresponding author. Tel.: +1 540 231 8231; fax: +1 540 231 5022.
E-mail address: emarand@vt.edu (E. Marand).

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sorption measurements on these membrane samples are performed in the non-humidified and humidified state over a temperature range of 25–75 °C at a constant pressure of 1 bar to gauge the impact the presence of water has on gas sorption behavior.

2. Experimental

2.1. Materials

The synthesis of the unsulfonated Diels–Alder poly(phenylene) (SDAPP0) has been documented by Fujimoto et al. [11]. The polymer is formed by the Diels–Alder condensation reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone)-benzene with diethnylbenzene. This reaction allows for a wide range of functionalities and configurations allowing the poly(phenylene) to be modified to achieve optimal properties desired for PEMs. To achieve sulfonation, the SDAPP0 solution is mixed dropwise with chlorosulfonic acid diluted with chloroform. The resulting precipitate is converted to the salt form (SDAPP) by adding 0.5 M NaOH and allowed to react at room temperature for 12 h. The comparable Nafion@ 112 was purchased commercially from Ion Power, Inc.

2.2. Membrane preparation

The SDAPP membranes were fabricated according to the following procedure. The sodium salt form of SDAPP was dissolved in dimethylacetamide (DMAc) at room temperature and stirred until the solution was clear and ready for casting. The concentration of the solution was approximately 5 wt% for casting on glass and 20 wt% when using the continuous casting process. The casting solutions were then filtered through an air-operated syringe filtering system using PTFE syringe filters at an air pressure between 30 and 40 psi. After filtration, the solutions were degassed in a vacuum oven for a minimum of 4 h before being cast.

The SDAPP 2.2 solution was cast onto a glass plate and placed in an oven under N_2 flow at 90 °C. After approximately 20 h, the film was removed from the glass plate and immersed in a deionized water bath at 100 °C for 1 h to remove any excess DMAc. The SDAPP 1.6 solution was processed by a continuous film casting method, using a lab reverse roll casting system [17]. The film caster consisted of a coating roll, a backing roll, and a stationary metering roll. The substrate belt was made of stainless steel and was driven by a pair of nip rolls, which could be adjusted for the desired casting speed to avoid defects. Typical film dimensions consisted of a thickness between 25 and 50 μm and a length of 4 ft. Once cast, the films were allowed to dry on top of a hot plate at a temperature of 50–80 °C. The films were then peeled from the substrate and dried in a vacuum oven. Both, the SDAPP 2.2 and SDAPP 1.6 polymer films were subsequently converted to their proton form by immersing the films in a 0.5 M H_2SO_4 at 100 °C for 1 h. These films were then rinsed thoroughly with deionized water and then submerged in a deionized water bath at 100 °C for 1 h to remove any residual acid. Nafion 112 samples were immersed in a deionized water bath at 80 °C for 2 h prior to use.

2.3. Proton conductivity measurements

Proton conductivity was measured with a Hewlett–Packard 4129 impedance/gain-phase analyzer over the frequency range of 10 Hz to 1 MHz. The membrane resistance was taken at the frequency corresponding to the minimum imaginary response. The conductivity, σ, was calculated from the measured membrane resistance (R), the distance between the two electrodes (l), and the cross-sectional area perpendicular to the proton flow (A). This relationship can be expressed as $\sigma = l/RA$ with units of S/cm [18,19].

Table 1
Membrane water dependence for SDAPP 1.6, SDAPP 2.2, and Nafion 112.

	IEC[a] (mequiv/g)	Water uptake[b] (wt %)	Proton conductivity[c] (S/cm)
SDAPP 1.6	1.6	56	0.074
SDAPP 2.2	2.2	137	0.123
Nafion 112	0.91	19	0.11

[a] IEC = $(1000/MW_{repeatunit}) \times$ degree of sulfonation $\times 2(\text{–}SO_3H)$.
[b] Water uptake $= \frac{W_{wet}-W_{dry}}{W_{dry}} \times 100\%$.
[c] Impedance spectroscopy in liquid water at 30 °C.

2.4. Gas permeation characterization

The H_2 and O_2 gas permeabilities of the disulfonated poly(arylene ether sulfone) copolymer and Nafion 112 were determined using a constant volume permeation apparatus [20]. A 2.5″ circular sample was cut from each membrane sheet and used in the permeation measurement. The films were masked with aluminum tape and sealed with epoxy to prevent leaks [21]. Gases were used as received from Air Products and possessed a purity of 99.99%. The feed pressure and temperature were kept constant at 1 atm and 35 °C, respectively, in all experiments. Each gas was run through a membrane three times and the average permeability and the standard deviation were recorded. The solubility parameter was calculated by the well-known time-lag method [22].

2.5. Gas sorption characterization

Sorption studies were performed using the gravimetric system (IGA-002, Hiden Isochema, UK). All chambers and tubing were degassed by applying a vacuum ($P \leq 10^{-4}$ mbar). Oxygen gas with 99.99% purity was passed through a molecular sieve before being supplied to the gravimetric system. Relative humidity was introduced into the gravimetric system using a two-gas feed system. One feed consisted of a dry oxygen gas and the other oxygen gas stream was piped through a stainless steel deionized water bath. The water bath had an upper temperature limit of 80 °C. These two streams mixed at the exit of the water bath. The percentage of wet flow in the feed stream was set by the temperature of the vapor generator and the relative flow rates of the dry and wet gas streams.

3. Results

3.1. Material properties

Table 1 compares the ion exchange capacity, IEC, water uptake as a weight percentage, and proton conductivity of SDAPP series to that of Nafion 112. The SDAPP samples have a larger ion exchange capacity than Nafion, i.e. higher sulfonic acid content, which leads to the increase in the water uptake. The proton conductivity in the SDAPP 1.6 sample is lower than that of Nafion 112. The SDAPP 2.2 has slightly higher proton conductivity than Nafion 112 due to the presence of more sulfonic acid groups.

3.2. Gas permeability measurements

The samples were soaked in deionized water, removed from the bath and any excess water was blotted from the surface. These

Table 2a
Gas permeability in Barrers for the respective polyelectrolyte membranes under fully hydrated conditions.

	Hydrogen (Barrers)	Oxygen (Barrers)
SDAPP 1.6	49.31 ± 2.04	6.83 ± 0.20
SDAPP 2.2	8.63 ± 0.76	0.57 ± 0.04
Nafion 112	8.14 ± 0.10	1.23 ± 0.04

Table 2b
Pure oxygen solubility in SDAPP series and Nafion under fully hydrated conditions.

	O_2 solubility (cc@STP/cc-atm)	% O_2 mass uptake
SDAPP 1.6	0.55	0.065
SDAPP 2.2	0.39	0.04
Nafion 112	0.06	0.005

samples were immediately inserted into the permeation cell. The change in dimensions of the membranes during the time-frame of the measurement was not significant to effect the absolute value of the permeability. Membranes having lower O_2 permeability than that of Nafion@ 112 are desirable, because during a proton exchange operation more O_2 gas can react at the cathode. Permeation results shown in Table 2a, indicate a similar H_2 gas permeability for SDAPP 2.2 as compared to Nafion@ 112, but a reduction for O_2. The bulky, pendant benzene groups allow the relatively small hydrogen to permeate through the membrane at a rate similar to that of Nafion@. However, the pendant benzene groups have π–π interactions which may hinder O_2 permeability [23]. The H_2 and O_2 permeability for SDAPP 1.6 is significantly higher than that of Nafion@ and SDAPP 2.2 because of differences in sample preparation. Gas permeabilities in polymers are highly sensitive to variations in densities, residual solvents and physical aging due to processing [16]. The SDAPP 1.6 sample used for gas permeability measurements was prepared using a film coater operating at elevated temperature, while the SDAPP 2.2 and Nafion@ samples were prepared by solvent casting method with subsequent complete removal of solvent. Processing at elevated temperatures of SDAPP 1.6 may have led to incomplete physical aging in the experimental time-frame, leading to a more open structure and higher permeabilities.

Table 2b compares the O_2 solubility in the SDAPP and Nafion 112 systems as measured by the time-lag method [24] in units of cc@STP/cc·atm and also as percent O_2 mass uptake as measured by equilibrium gravimetric sorption. Clearly, the O_2 sorption is much higher in both SDAPP 1.6 and SDAPP 2.2 than in the Nafion. Since the overall O_2 permeability in the SDAPP 2.2 is lower compared to that in Nafion, and permeability is the product of solubility and diffusion, this suggests that the permeability in the SDAPP 2.2 is indeed diffusion controlled.

3.3. *Gravimetric sorption measurements*

Gravimetric sorption measurements in Nafion 112 and SDAPP membranes were carried out as a function of pressure from 0 to 10 bar, temperature from 25 °C to 75 °C and relative humidity from 0 to 80% RH. Fig. 1 displays the O_2 pressure isotherms for (a) SDAPP 1.6, (b) SDAPP 2.2 and (c) Nafion 112 samples under dry conditions. At low temperatures, the O_2 sorption isotherms in all samples follow Henry's Law type behavior, which permits the enthalpy of solution to be calculated by linearly fitting the variation of solubility, *S*, vs. temperature, *T*. The isotherms at 60 °C and 75 °C also display a plateau across 2000 mbar. This behavior could be attributed to the α or β relaxation transitions of polymer containing ionic group aggregates [25]. Otherwise, at higher pressures where the sorption

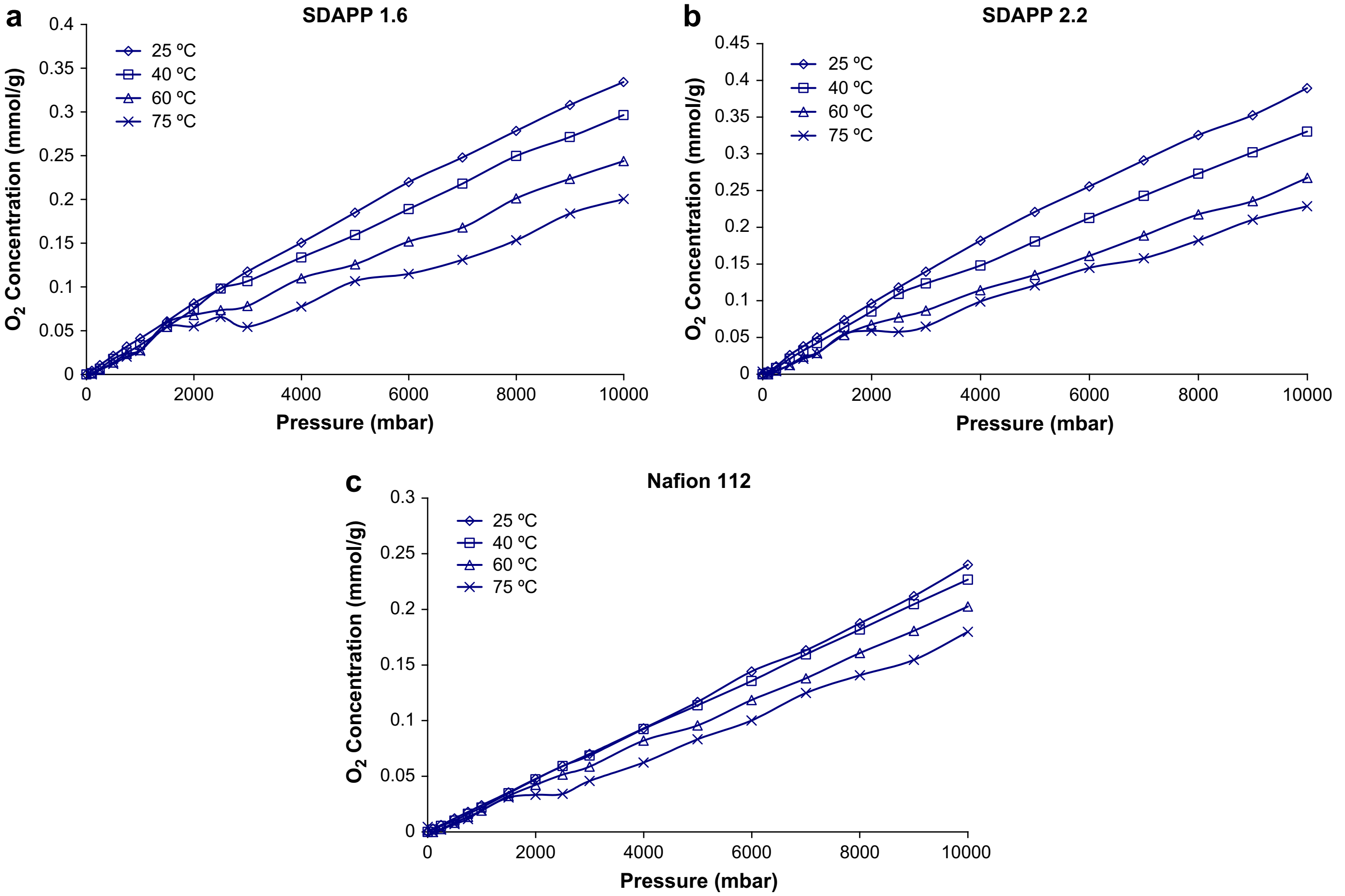

Fig. 1. Non-humidified pressure O_2 sorption isotherms for (a) SDAPP 1.6 (b) SDAPP 2.2 and (c) Nafion 112 over a temperature range of 25–75 °C.

Table 3
Enthalpy results for the SDAPP 1.6, SDAPP 2.2, and Nafion 112 membranes at 0% relative humidity. ΔH_s reported with an error of ±0.5 kJ/mol.

	8000 (mbar)	9000 (mbar)	10,000 (mbar)
SDAPP 1.6			
ΔH_s (kJ/mol)	−10.0	−8.8	−8.7
S_o (mmol/g)	0.01	0.01	0.01
SDAPP 2.2			
ΔH_s (kJ/mol)	−10.0	−9.2	−9.2
S_o (mmol/g)	0.01	0.01	0.01
Nafion 112			
ΔH_s (kJ/mol)	−5.0	−5.4	−4.9
S_o (mmol/g)	0.03	0.03	0.03

behavior is linear, the solubility can be related to temperature by a van't Hoff relationship expressed in Equation 1 [26]:

$$S = S_o \exp\left(\frac{-\Delta H_s}{RT}\right) \tag{1}$$

where S_o is a constant, R is the ideal gas constant, T is temperature, and ΔH_s is the partial molar enthalpy of sorption. ΔH_s has two contributions as expressed by Equation 2 [27,28]:

$$\Delta H_s = \Delta H_{cond} + \Delta H_{mix} \tag{2}$$

where ΔH_{cond} is the change in enthalpy associated with a penetrant going from the gas state to a condensed state and ΔH_{mix} is the enthalpy change associated with creating a gap for the a gas molecule to dissolve in the membrane. In the case of small molecules with low molecular weight and low critical temperatures, ΔH_{cond} is small and ΔH_s is dominated by the ΔH_{mix} term. When weak interactions between the polymer and gas occur, ΔH_{mix} is negative causing a decrease in solubility with increasing temperature [28]. In the case of the SDAPP series, the solubility of O_2 clearly decreases with temperature. Table 3 displays negative ΔH_s values as calculated from Equation 1 at three different pressures. We postulate that the ΔH_s values for the SDAPP membranes are more negative than those calculated for Nafion because the higher ion exchange capacity in the SDAPP membranes leads to more O_2–HSO_3 interactions [29]. The absolute value of ΔH_s decreases with increasing pressure, which further supports the idea of the presence of molecular interactions between the oxygen molecules and the sulfonic acid groups in the polymer membranes [30]. These interactions decrease with increasing O_2 pressure as the environment into which the O_2 dissolves includes more oxygen clusters. Furthermore, as the temperature increases, these interactions are disrupted and the solubility drops.

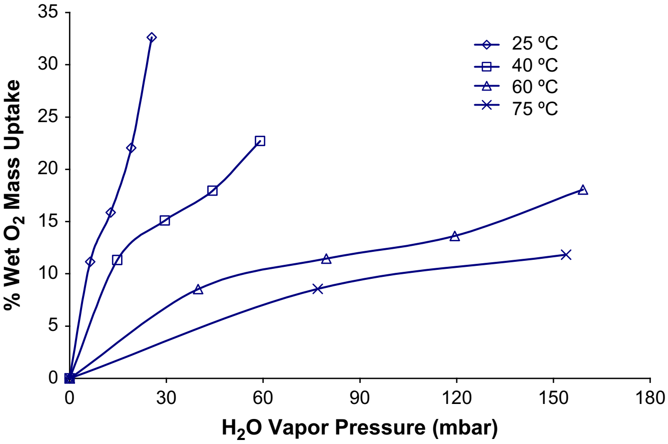

Fig. 3. O_2 sorption isotherm for SDAPP 2.2.

As mentioned in the introduction, water inside a fuel cell is necessary to facilitate the transport of ions. Similarly, one would expect that the transport of O_2 depends on the presence of water and its physical state, i.e. whether the water molecules are self-associated or hydrogen bonded to the polymer. Experiments were carried out to determine the percent of wet-O_2 mass uptake (oxygen in the presence of water) as a function of temperature and relative humidity at a total pressure of 1 atm. The introduction of relative humidity is expected to dramatically change the O_2 sorption behavior in all samples. Since the moisture content in the incoming O_2 wet stream also varies with temperature, in order to compare isothermal sorption, the results are reported as a function of the water's vapor pressure at the respective temperature. The vapor pressure is directly proportional to the product of relative humidity and the saturation pressure. The saturation pressure was calculated from the Antoine's Equation [31] Figs. 2–4 display the wet mass uptake of O_2 for all membranes at 1 atm total pressure as a function of vapor pressure of H_2O.

In all cases, the percent wet-O_2 mass uptake increased with increasing vapor pressure. The rate of increase in the wet-O_2 mass uptake is higher at low temperatures. At low temperatures there is also the appearance of Type IV sorption, also called the Brunnauer, Emmett and Teller (BET) sorption [28]. Type IV sorption is the sum of Type II (Langmuir) and Type III (Flory–Huggins) sorptions, and is

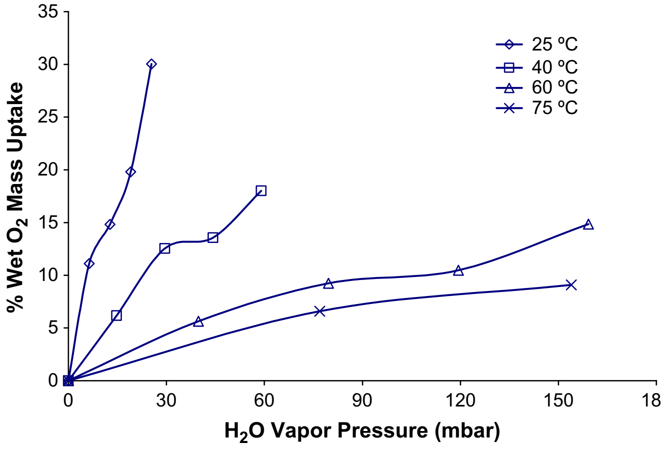

Fig. 2. O_2 sorption isotherm for SDAPP 1.6.

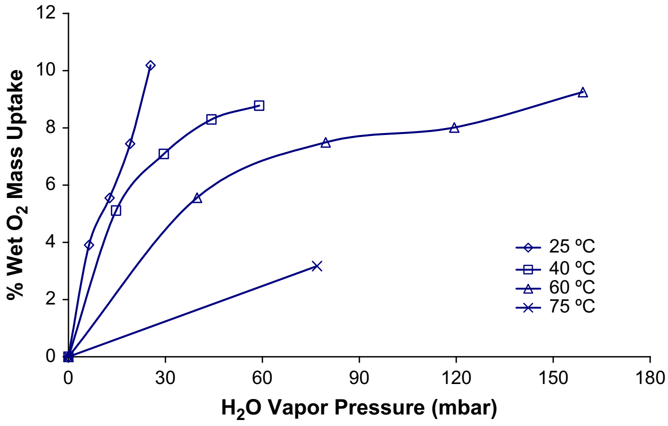

Fig. 4. O_2 sorption isotherm for Nafion 112.

typical of water sorbing in a highly hydrophilic polymer. The initial rise in sorption (at low H_2O vapor pressure) can be attributed to the water hydrating the sulfonic acid groups. Once saturation of the membrane occurs, swelling takes place at higher H_2O vapor pressures (higher RH) and causes the sorption to increase even further [32]. The resulting increase in free volume should aid gas transport. Since O_2 and H_2O sorptions are coupled in these experiments, it is difficult to separate their individual contribution to the overall sorption. However, comparing the separate solubilities of O_2 in the polymer, water, and the polymer/water systems can provide some insight. From Fig. 1a, the solubility of pure O_2 in the dehydrated SDAPP 2.2 at 1 atm and 25 °C is 0.05 mmol/g or 0.16 wt% O_2 uptake. From literature, the solubility of O_2 in water at 25 °C is 7.2×10^{-4} mmol/g [23], which is quite low in comparison to O_2 sorption in the dry SDAPP. Interestingly, the solubility of O_2–water system in the SDAPP 2.2 polymer is only 0.013 mmol/g or percent wet-O_2 uptake of 0.042 wt%. Furthermore, this wet-O_2 mass uptake value is significantly lower than the liquid water uptake value of 137 wt% found in Table 1. Since the sorption of O_2 in the water is relatively low, it is possible that the combined water–oxygen sorption is actually dominated by the sorption of water vapor in the polymer.

Figs. 2–4 also show that as the temperature increases, the percent wet-O_2 mass uptake decreases. A review by Moore and Mauritz [33] suggests that water may condense on the membrane surface with more difficulty at higher temperatures and therefore lower the total sorption [33]. When comparing Figs. 2–4, it is quite evident that the total mass uptake of wet O_2 in the SDAPP samples is much higher that that observed in Nafion. One possibility is that the presence of water facilitates sorption of O_2 into the polymer system. This effect seems to be greater in the SDAPP materials than in the Nafion because of their higher ion exchange capacity.

4. Conclusions

The transport behavior of H_2 and O_2 gases in a Diels–Alder synthesized poly(phenylene) was compared to the transport behavior in Nafion. The presence of moisture dictated the sorption behavior. Under dry conditions, the sorption of O_2 in both SDAPP and Nafion membranes showed Henry's law behavior. In the presence of humidity and low temperatures, the sorption isotherms followed Type IV behavior. This suggests the formation of hydrogen bonding between the sulfonic acid groups in the membrane and the water, thus leading to polymer swelling. The presence of water in the SDAPP membrane facilitated a larger O_2 sorption in the SDAPP materials when compared to Nafion 112.

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