

MIT Open Access Articles

Free Volume Enhanced Proton Exchange Membranes from Sulfonated Triptycene Poly(Ether Ether Ketone)

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Moh, Lionel C.H. et al. "Free volume enhanced proton exchange membranes from sulfonated triptycene poly(ether ketone)." *Journal of Membrane Science*, 549 (March 2018): 236-243.

As Published: <http://dx.doi.org/10.1016/j.memsci.2017.11.041>

Publisher: Elsevier BV

Persistent URL: <https://hdl.handle.net/1721.1/123895>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-NonCommercial-NoDerivs License



Free Volume Enhanced Proton Exchange Membranes from Sulfonated Triptycene Poly(Ether Ether Ketone)

*Lionel C.H. Moh, John B. Goods, Yoonseob Kim, Timothy M. Swager**

Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Keywords: PEMFC, proton exchange membrane, sulfonated PEEK, free volume, triptycene

Abstract

A triptycene based poly(ether ether ketone) (tripPEEK) was synthesized and sulfonated to form proton exchange membranes. The increase in intrinsic free volume resulting from the incorporation of sterically bulky triptycene moiety, imparts high affinity to water at all levels of relative humidity (RH) from 10 %RH to 90 %RH. S-tripPEEK membranes showed proton conductivities of 334 mS/cm at 85 °C at 90 %RH and 0.37 mS/cm at 85 °C at 20 %RH. Membranes of similar ion exchange capacity (IEC) are compared to deconvolute the effect of free volume from IEC in enhancing proton conductivity. Increasing the free volume of the membranes increases the proton conductivity and decreases the activation energy for proton conduction between 10 %RH to 90 %RH.

Introduction

Proton exchange membranes (PEMs) are a critical component of electrochemical energy storage devices such as fuel cells. Currently, the most widely used PEMs are composed of perfluorinated poly(sulfonic acids), such as NafionTM, wherein protons transported via proton transfer between sulfonic acid groups and water molecules in channels that are generated by the

directed assembly of the hydrophobic fluorinated polymer structure. Nafion's chemical stability and excellent ionic transport properties are well known and extensively reviewed, [1,2] but high cost of production and reduced proton conductivities after exceeding temperatures 80 °C are significant limitations to this material.[3–10] One of the promising alternative polymeric systems to solve those problems is sulfonated poly aryl ethers.[3–7] Sulfonated poly aryl ethers can be polymerized through reactions with low cost reactants and are thermally and chemically stable at temperatures above 80 °C. Fuel cells operating at temperatures above 80 °C are more efficient due to lower carbon monoxide poisoning of the platinum catalyst and reduce the need for cooling systems on the fuel cell. [11–13]

In these sulfonic acid-based proton exchange membranes, mechanistic and empirical studies have shown that water is instrumental in fast proton conduction.[2,8,10,11,14–19] The amount of water in these membrane is closely related to the hydration of hydrophilic sulfonate groups. In Nafion, hydrophilic sulfonate groups in the polymer coalesce, creating nanopores with high affinity for hydration, which form a percolated water network for proton conduction. At high temperatures and low relative humidity, water is lost to the environment and the nanopores collapse, resulting in a drastic decrease in proton conductivity.

One way to address the loss of water at low humidity and high temperature is to increase intrinsic free volume within the membrane. Intrinsic free volume can be introduced by adding bulky groups to sulfonated poly aryl ethers through rigid side chains,[9,20,21] chain branching,[22] or by introducing bulky groups into the polymer backbone.[23–26] When the polymer membrane is completely dried, these rigid bulky groups prevent packing and produce nanopores. However,

this is accompanied by stress to the material that results in distorted bond angles and an increase in internal energy.[9] This internal energy is relieved when the membrane is exposed to small molecule solvents that can fill the pores and plasticize the polymer. Since water molecules are plasticizers for sulfonate polymers that are hydrophilic, it is energetically favorable for polymers with bulky groups to retain more water molecules at low humidity to prevent the energetic penalty from drying the membrane and thus retain a higher proton conductivity.

Although proton conductivity enhancements have been seen in the aforementioned earlier work, studies are lacking to best understand the factors that affect proton conductivity, including the ion exchange capacity (IEC), with a systematic control of free volume in the membranes. In this contribution, we report the use of the triptycene moiety to systematically control the intrinsic free volume in a PEEK-based PEM. The triptycene group increases the free volume in the polymer as a result of the three dimensional non-compliant triptycene group[27–29] and the phenyl rings associated with this structure allow for simple post polymerization sulfonation wherein the degree of sulfonation can be easily controlled. By synthesizing random copolymers with different number of triptycene groups and controlling the degree of sulfonation, membranes with similar IEC but different amounts of free volume were directly compared to elucidate the effect of free volume on proton conductivity. This serves as a guide to new designs for PEMs that can be used at low humidity and high temperature.

Experimental

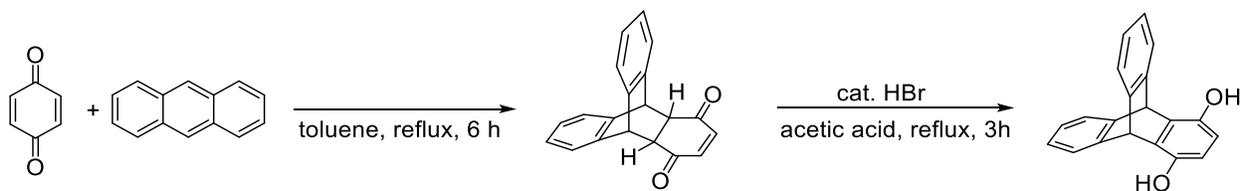
Materials:

Anthracene, benzoquinone, hydrobromic acid, hydroquinone, 4,4'-difluorobenzophenone and anhydrous potassium carbonate was purchased from Sigma Aldrich and used as received. Glacial acetic acid was purchased from VWR and used as received. N,N'-dimethylacetamide (DMAc) and toluene were dried over 3 Å and 4 Å molecular sieves for at least 48 hours.

Synthesis of triptycene hydroquinone:

Triptycene hydroquinone was synthesized according to literature.[26,30] Anthracene (35.65g, 200 mmol) and 1,4-benzoquinone (21.62g, 200 mmol) in 200 ml of toluene were heated under reflux for 6 h and cooled to room temperature. The precipitated triptycene benzoquinone was filtered and washed with toluene and dried in a vacuum oven at 75 °C overnight. Triptycene benzoquinone was then added to 300 ml of glacial acetic acid and was heated under reflux. 1 ml of 40% hydrobromic acid was slowly added to the reaction and the reaction was left to stir under reflux condition for 3 h and left to cool to room temperature, precipitating triptycene hydroquinone that is filtered and dried in the vacuum oven at 75 °C overnight. Triptycene hydroquinone was obtained in 65% yield over two steps. ¹H NMR (400MHz, DMF-d7, 293K): 9.02 (2H, s), 7.44 (4H, m), 7.00 (4H, m), 6.42 (2H, s), 5.96 (2H, s); ¹³C NMR (100MHz, DMF-d7, 293K): 147.38, 146.52, 133.48, 125.82, 124.64, 114.08, 48.43.

Scheme 1. Synthesis of triptycene hydroquinone



Synthesis of Triptycene Poly(Ether Ether Ketone) (tripPEEK(x,y)):

TripPEEK and its copolymers, designated tripPEEK(x,y) (Table 1), were synthesized through aromatic nucleophilic substitution (S_NAr) reaction between x equivalents of triptycene hydroquinone, y equivalents of hydroquinone and (x+y) equivalents of 4,4'-difluorobenzophenone (Scheme 2). The general procedure of polymerization, illustrated using tripPEEK(1,3), is as follows: In a flamed dried two-necked round bottom flask under nitrogen atmosphere with a Dean-Stark apparatus, triptycene hydroquinone (2.863 g, 10.0 mmol), hydroquinone (3.303 g, 30.0 mmol) and 4,4'-difluorobenzophenone (8.728 g, 40.0 mmol) was dissolved in anhydrous DMAc (80 ml) and anhydrous toluene (10 ml). Potassium carbonate (12.715 g, 23.0 mmol) was added and the reaction was heated to 140 °C for azeotropic distillation to remove water that was generated in the reaction. Once all the toluene was collected the reaction was heated under reflux conditions (165 °C) for 18 hours. The reaction was then precipitated in boiling water and filtered. The resulting polymer was purified by dispersing in boiling DMAc and precipitating twice in boiling water and twice in methanol. The resultant polymer was further purified with a Soxhlet extraction with acetone two days, yielding an off-white polymer powder that was dried in the vacuum oven for two days at 75 °C.

Scheme 2. Polymerization of TripPEEK(x,y) through SNAr reaction

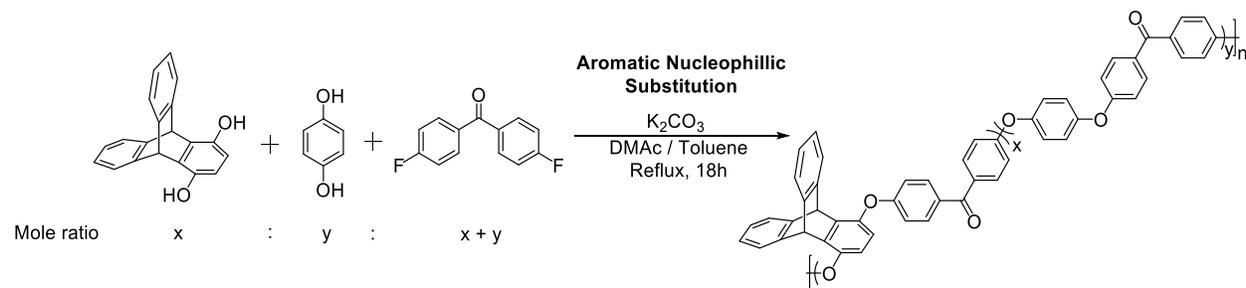


Table 1. Mole ratio of monomers of polymers. Average molecular weight per repeat unit is calculated in equation below

Designation	Mole ratio			Average molecular weight per repeat unit (g/mol)
	triptycene hydroquinone (x)	hydroquinone (y)	4,4'-difluorobenzophenone (x+y)	
tripPEEK(1,0)	1	0	1	464.5
tripPEEK(1,1)	1	1	2	376.4
tripPEEK(1,3)	1	3	4	332.4
PEEK	0	1	1	288.3

$$\text{Ave. Molecular Weight per repeat unit} = \frac{x(464.5) + y(288.3)}{x + y}$$

Synthesis of sulfonated tripPEEKs (S-tripPEEK) and sulfonated PEEK (S-PEEK):

TripPEEK and PEEK were sulfonated with concentrated sulfuric acid. 0.5g of polymer was stirred in 10 ml of concentrated sulfuric acid for 4 hours to dissolve the polymer before the solution was heated to 65 °C and left to stir for 1 hour. The degree of sulfonation can be increased with a longer reaction time at 65 °C. Sulfonated polymers were precipitated in ice water, filtered and rinsed with deionized water and transferred into a dialysis tubing (Molecular weight cut off of 10000 Da) for dialysis with deionized water until pH neutral.

Formation of proton exchange membranes:

S-trpPEEKs and SPEEK were dissolved to form 10 wt% solutions in dimethylformamide. 2.0 ml of the polymer solution was dispensed on a 75 mm × 25 mm glass slide and heated to 75 °C for 2 hours before drying overnight under vacuum at 75 °C. Free standing membranes with thicknesses between 100-150 μm were peeled off the glass slides and cut to sizes needed for further experiments. The membranes were soaked in 2.0 M sulfuric acid for 24 hours to protonate the membranes. Thereafter, the membranes were transferred into deionized water and soaked for 24 hours, replacing the deionized water every 8 hours to remove residual acid.

Pretreatment of Nafion 117:

Nafion 117 membranes were pretreated as reported in literature [10] to remove organic impurities and reprotonate all sulfonic acid groups before all measurements. Nafion 117 membranes were boiled in a 3% H₂O₂ aqueous solution for 1 hour, rinsed with deionized water and boiled in a 0.5 M sulfuric acid solution for 1 hour. The protonated membranes were then soaked in deionized water for 24 hours, switching the deionized water every 8 hours, to remove residual sulfuric acid. The pretreated membranes were then kept in deionized water before testing.

General characterization methods:

¹H NMR spectra were obtained using a Bruker 400MHz. Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectra were determined and baseline corrected using a Nexus Model 470/670/870 Spectrophotometer using the Omnic software package. Molecular weights of TripPEEKs were obtained with the soluble fraction in THF using gel permeation chromatography with polystyrene as a standard. Absolute molecular weights of S-tripPEEKs were determined by gel permeation chromatography using an Agilent LC system with a Wyatt

miniDAWN TREOS multi-angle light scattering detector and DMF (doped with 0.02 M LiBr) as eluent. Thermogravimetric analysis was performed using TA instrument TGA Q5000 from 25 °C to 900 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed using a TA instruments Q1000 at a heating and cooling rate of 10 °C/min.

Ion exchange capacity:

Ion exchange capacity (IEC) was determined by titration with 0.01 M sodium hydroxide solution. Membranes were soaked in 2.0 M HCl overnight to protonate all sulfonate groups. Protonated membranes were rinsed with deionized water 3 times and soaked in 2.0 M NaCl solution overnight for ion exchange. The solution was then titrated with 0.01 M (M_{NaOH}) sodium hydroxide solution (standardized with 0.010 M potassium hydrogen phthalate) until pH 7.0 using a pH meter and the volume of base (V_{NaOH}) was used to calculate IEC with equation below, where m_{dry} is the mass of dried membrane.

$$\text{IEC} = \frac{(V_{\text{NaOH}})(M_{\text{NaOH}})}{m_{\text{dry}}}$$

Water uptake and hydration number:

Water uptake (WU) and hydration number (λ) at 20 %RH were obtained through thermogravimetric analysis (TA instruments TGA Q5000). All measurements were done in triplicates and averaged.

Small pieces of S-tripPEEK membranes were first dried in a vacuum oven at 100 °C for 18 hours and removed to equilibrate at 20 %RH at room temperature over 48 hours. The

equilibrated film was heated in the TGA from 25 °C to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 2 hours. The mass loss below 150 °C was attributed to the loss of water and was used to calculate water uptake (WU) using equation below where $m_{25\text{ °C}}$ is the mass at 25 °C, $m_{150\text{ °C}}$ is the mass after holding at 150 °C for 2 hours.

$$\text{Water uptake (WU)(\%)} = \frac{m_{25\text{ °C}} - m_{150\text{ °C}}}{m_{150\text{ °C}}} \times 100\%$$

Hydration number, λ , which is defined as the number of water molecules for every sulfonate group can be calculated using the equation below, where $MW_{\text{H}_2\text{O}}$ is the molecular weight of water and WU is water uptake as reported in percent.[5]

$$\text{Hydration number } (\lambda) = \left(\frac{\text{WU}/100}{MW_{\text{H}_2\text{O}}} \right) \left(\frac{1}{\text{IEC}} \right)$$

Fractional free volume of PEMs:

Fractional free volume (FFV) is defined as the fraction of volume in PEMs that is not occupied by the polymer and is determined using the equation below where V is specific apparent volume of the PEM and V_0 is specific skeletal volume of the polymer.

$$\text{FFV} = \frac{V - V_0}{V}$$

To obtain the specific volumes needed, before any measurements, all PEMs were dried in a vacuum oven at 85 °C for over 20 hours and quickly placed into a dessicator after drying to cool to room temperature to prevent adsorption of atmospheric water. Polymers were then weighed quickly with a microbalance (Mettler Toledo) to obtain the dry mass (m_{dry}).

Specific apparent volume (V) of the PEMs were calculated based on mass and dimensions of the dry PEM using the equation below. Thicknesses (t) were measured using a Mitutoyo micrometer and averaged over 9 locations on the membrane. Lengths (l) and widths (w) were measured using a Mitutoyo digital calipers and averaged over 3 locations on the membrane. Both the micrometer and digital calipers have been calibrated by the manufacturer and comes with a NIST traceability certificate.

$$V = \frac{(t)(l)(w)}{m_{\text{dry}}}$$

Specific skeletal volume (V_0) of polymers were obtained via helium pycnometry (Micromeritics AccuPyc II 1340). The dried membranes were quickly loaded into the pycnometer to obtain the corresponding skeletal volume (V_{dry}). Helium pycnometry was done at 19.5 psi helium with 4 purge cycles and averaged over 5 measurements. V_0 was then calculated using the equation below.

$$V_0 = \frac{V_{\text{dry}}}{m_{\text{dry}}}$$

Proton conductivity measurements:

Proton conductivity (σ) at various humidity and temperature was obtained through electrochemical impedance spectroscopy (EIS) using a Biologic SP 200. Films were placed across 2 platinum electrodes spaced 3 cm apart. The spacing of 3cm was chosen as proton conductivity measured from two-probe measurements at electrode distances above 2.7cm are similar to four-probe measurements, minimizing the variance between the two configurations. [31]

For proton conductivity in water, the setup is placed in a water bath at 20 °C. For proton conductivity at different relative humidity, the setup is placed in a humidity chamber (Espec BTL433). All membranes were tested with the same heating and cooling profile where membranes were measured at the highest relative humidity (90 %RH) first, starting from 85 °C and cooling down to 25 °C in 10 °C step and equilibrating for 1 hour before each measurement. For relative humidity below 30 %RH, the membranes were tested from 85 °C to 60 °C in 5 °C steps due to limitations in the dehumidifier of the humidity chamber.

Measurements were done in Potentio Electrochemical Impedance Spectroscopy (PEIS) mode with a mean AC voltage 0 V and an amplitude of 0.1 V over a frequency range of 1MHz to 0.1 MHz. The high frequency intersect between the curve and the real axis of the Nyquist plot was recorded as bulk resistance of the membrane (R). Proton conductivity (σ) was then calculated using equation below where l is the length between the electrodes, w is the width of the membrane and t is the thickness of the membrane. All dimensions were measured at 20% RH. Activation energy was calculated based on an Arrhenius relation.

$$\sigma = \frac{l}{(R)(t)(w)}$$

$$\sigma = Ae^{-\left(\frac{E_a}{RT}\right)}$$

Results and Discussion:

Physical properties of tripPEEKs:

Comparing tripPEEKs with PEEK showed that the inclusion of the triptycene moiety added steric bulk which prevented π -stacking and inhibited crystallization, as observed in PEEK (Figure 1). DSC thermograms of all tripPEEKs showed only a single glass transition and no melting

transition, suggesting that (i) tripPEEK(1,1) and tripPEEK(1,3) are random copolymers and (ii) tripPEEKs do not crystallize. The absence of a crystalline phase makes tripPEEKs more soluble than PEEK and allows for solubility in common organic solvents, such as chloroform, dichloromethane and boiling polar solvents, such as dimethylacetamide and dimethylformamide. A benefit of the relative solubility of tripPEEKs is that ^1H NMRs can be obtained. With enhanced solubility, tripPEEKs polymerizes to a high molecular weight which soluble fractions have a number average molecular weight of more than 100 kDa with respect to polystyrene standards. High molecular weights in tripPEEKs allow for good film forming properties that are necessary to form free-standing membranes.

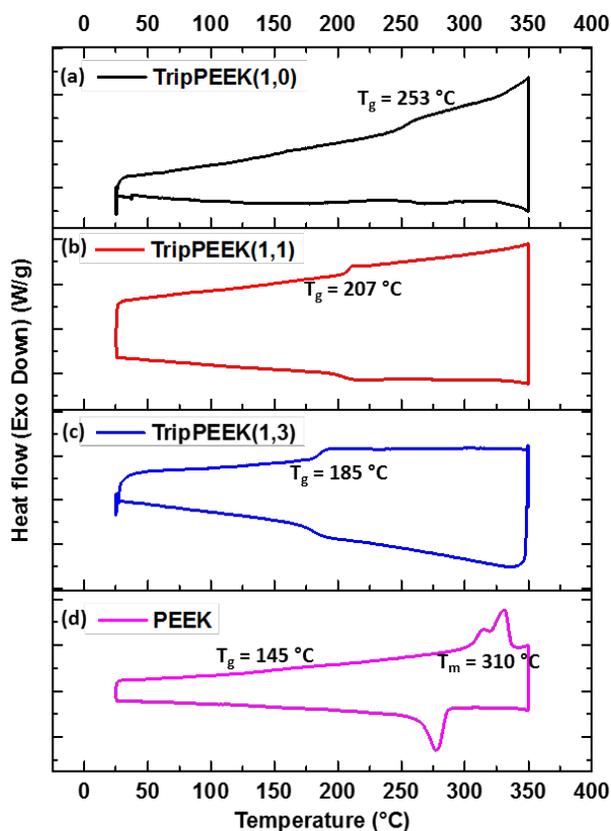


Figure 1. DSC thermograms of (a) tripPEEK(1,0), (b) tripPEEK(1,1), (c) tripPEEK(1,3) and (d) PEEK. Heat flows are measured from 25 °C to 350 °C at a heating and cooling rate of 10 °C/min.

In addition to enhanced solubility, triptycene moieties also affect the density of the tripPEEK polymers (Table 2). Since the triptycenes increase the free volume in the material, it was expected that with more of the triptycene moiety present, the density will be lower. However, since adding triptycene moieties also increases the mass of repeating unit, the net effect resulted in the density of tripPEEK(1,0) being higher than tripPEEK(1,1). By normalizing the densities with the average molecular weight of a repeating unit, the volume per mole of repeating unit shows that with more triptycene in the polymer the higher the volume per repeat unit is obtained, suggesting that triptycene can contribute to additional volume in each repeat unit.

Table 2. Densities and volume per repeat unit of tripPEEKs

	Average MW per repeat unit (g/mol)	Skeletal density (g/cm ³)	Volume/repeat unit (cm ³ /mol)
TripPEEK(1,0)	464.5	1.299	357.6
TripPEEK(1,1)	376.4	1.276	295.0
TripPEEK(1,3)	332.4	1.327	250.5
PEEK	288.3	1.321	218.2

Properties of sulfonated tripPEEKs (S-tripPEEK):

The sulfonation of tripPEEKs using concentrated sulfuric acid was successful as indicated by the new peaks in the IR spectra (Figure 2). The peaks at 1180 cm⁻¹ are assigned to the S=O stretch and 1050 cm⁻¹ from symmetric sulfonate group stretch.

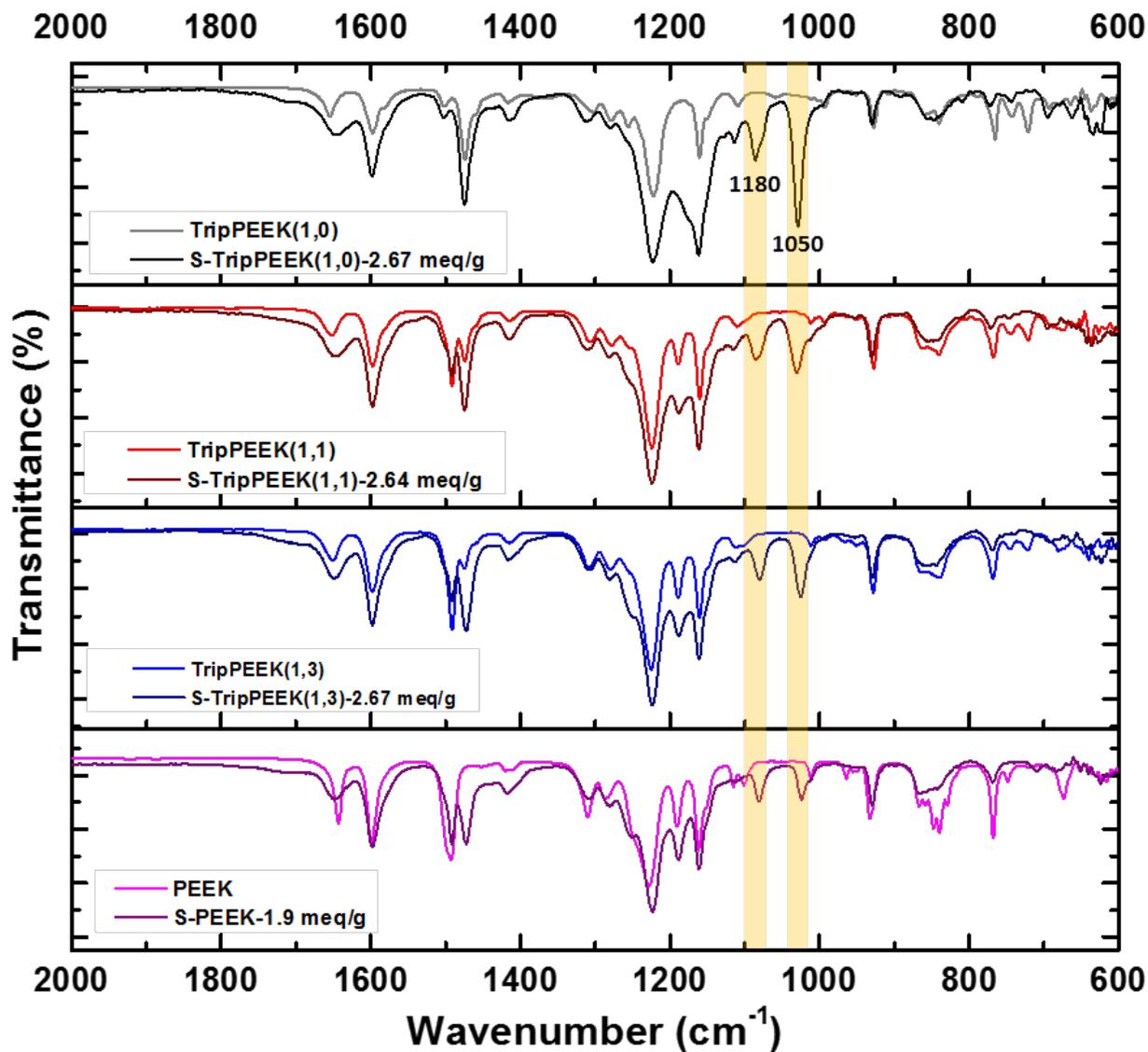


Figure 2. FTIR spectra for tripPEEKs and S-tripPEEKs. Peaks at 1180 cm^{-1} and 1050 cm^{-1} are vibrational peaks from the sulfonate group.

^1H NMR analysis of tripPEEK(1,0) and S-tripPEEK(1,0) (Figure 3) suggests that some of the sulfonate groups were added to the extended ‘wings’ of the triptycene group. Addition to the phenyl ring with the ether linkage would result in a lone proton that should integrate to 1, however the aromatic triptycene peaks integrated to 16 relative to the bridgehead protons, indicating that sulfonate groups are also added to the extended rings of the triptycene group. Sulfonation should

preferentially occur on the more electron rich ring with 1,4-diether linkages, but since concentrated sulfuric acid is both a sulfonating reagent and solvent, this provides for aggressive sulfonation conditions that can add SO₃H groups to the other two phenyl rings of the triptycene. The ketone bearing phenyl rings are deactivated and the integration relative to the bridgehead protons indicates that under the conditions used no sulfonation occurs on these rings. It is known that electrophilic substitution of triptycene occurs in a sequential fashion when adding electrophilic groups,[27] and hence, should follow the same trend with sulfonation. The reduction in rate of addition with each sequential addition resulting in a slower rate is a result of homo-conjugation. As a result, the signal at approximately 7.05 ppm suggests that we have selectively sulfonated the electron rich ring and one other ring of the triptycene.

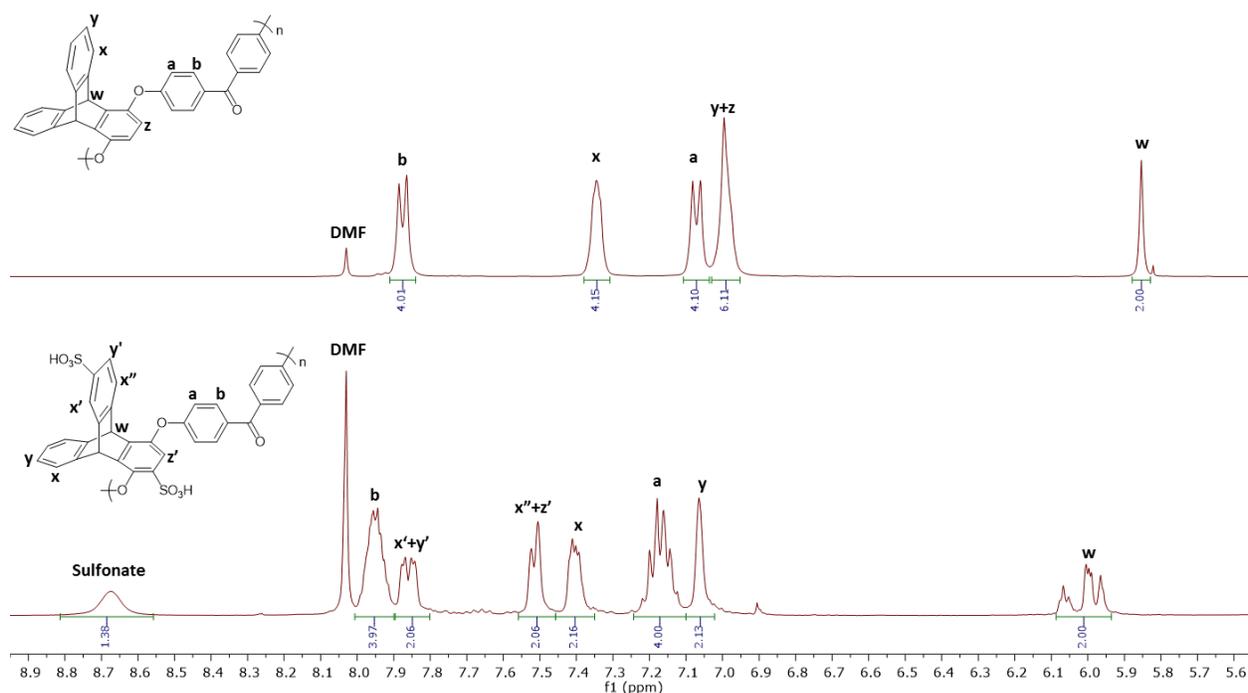


Figure 3. ¹H NMR of tripPEEK(1,0) and S-tripPEEK(1,0). S-tripPEEK was sulfonated with concentrated sulfuric acid at 65 °C for 1 hour, resulting in successful sulfonation of 2 out of the 3 phenyl rings on the triptycene group.

Thermogravimetric analyses of S-tripPEEKs and S-PEEK(Figure 4) showed an initial mass loss that is associated with the loss of water that is attached to the hygroscopic sulfonate groups. The mass loss at 350 °C was attributed to the decomposition of sulfonate groups. Hence, S-tripPEEKs are stable to 350 °C, which is well above the operating temperature of up to 200 °C in PEMFCs.[12,32]

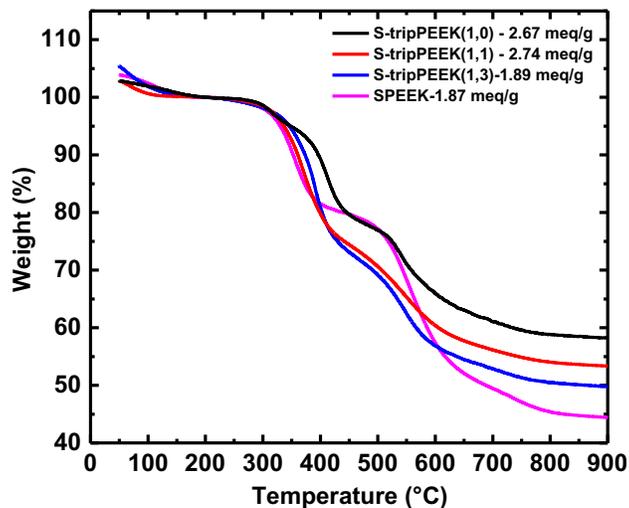


Figure 4. TGA of S-tripPEEKs and S-PEEK from 50 °C to 900 °C at a heating rate of 20 °C/min. TGAs are normalized such that 100% is weight percent after the mass loss associated to water.

As there are more sites available for functionalization with sulfonate groups in tripPEEKs compared to PEEK, S-tripPEEKs with a larger range of degrees of functionalization and thus different IECs were prepared for evaluation (Table 3). The table shows the corresponding molecular weights of the membranes with different IEC are listed. Aggressive sulfonation does result in some degradation of the polymer, as for each of S-tripPEEK(1,0), S-tripPEEK(1,1) and S-tripPEEK(1,3), higher degree of sulfonation resulted in a molecular weight reduction. Nonetheless, S-tripPEEKs maintain absolute molecular weight of the polymers in the range of 33-100 kDa and still produced robust free standing membrane for further testing.

Table 3. Range of molecular weight, IEC and degree of sulfonation of all S-tripPEEKs and SPEEKs made. Limits of IECs are listed with respect to the molecular weight of the corresponding polymer. High IEC, with high degree of sulfonation results in lower molecular weight of the polymer. Degree of sulfonation is defined as ratio of sulfonate groups to reactive phenyl ring.

	Mn (kg/mol)	Mw (kg/mol)	IEC (meq/g)	Degree of Sulfonation
StripPEEK(1,0)	60.5 – 85.2	103 – 146	3.35 – 2.67	0.67 – 0.53
StripPEEK(1,1)	35.5 – 77.0	50.3 – 136	2.79 – 2.64	0.66 – 0.63
StripPEEK(1,3)	33.9 – 61.8	64.8 – 91.5	2.67 – 1.89	0.75 – 0.52
SPEEK	40.5	62.3	1.87	0.63

Free volume enhanced proton conductivity:

Table 4 In an effort to deconvolute the effect of free volume and IEC on proton conductivity at various levels of relative humidity, S-tripPEEK(1,0), (1,1) and (1,3) membranes of similar IEC were chosen for a comparative study (Table 4). Similar to the corresponding tripPEEKs, the skeletal densities of S-tripPEEKs also do not necessarily decrease with increasing number of triptycene groups. Calculations for the volume per repeat unit again show increases with increasing ratios of triptycene moiety in the polymer, suggesting that the fluctuations in skeletal density are the result of the increase in mass contributed from the bulky triptycene groups. More importantly, the fractional free volume (FFV) was observed to increase with the number of triptycene moiety in the polymer. Since the dimensions used to calculate FFV are the same ones used for the calculation in proton conductivity, FFV is directly related to the amount of space water molecules can occupy within the membrane, which in turn affects the proton conductivity of the membrane.

Table 4. Properties of chosen S-tripPEEK membranes

	IEC (meq/g)	MW / repeat unit (g/mol)	Skeletal Density (g/cm ³)	Vol per repeat unit (cm ³ /mol)	V ₀ (cm ³ /g)	V (cm ³ /g)	FFV (cm ³ /cm ³)
S-tripPEEK (1,0)- 2.67	2.67	590.7	1.405	420	0.712	0.874	0.19

S-tripPEEK (1,1)- 2.64	2.64	477.2	1.380	346	0.724	0.855	0.15
S-tripPEEK (1,3)- 2.67	2.67	422.6	1.422	293	0.703	0.793	0.11

Proton conductivities of these membranes, as compared to SPEEK and Nafion 117 at 85 °C over the full range of relative humidity (Figure 5) show the enhancement in proton conductivity in S-tripPEEKs. At 20 %RH, S-tripPEEKs have proton conductivities of 0.02 – 0.4 mS/cm compared to Nafion 117 at 0.0014 mS/cm and SPEEK at 0.0015 mS/cm. Similarly at 90 %RH, S-tripPEEK membranes exhibit proton conductivities of 0.11 – 0.33 S/cm, as compared to Nafion 117 at 0.02 S/cm and SPEEK at 0.075 S/cm. Conductivities of Nafion 117 observed were lower than the optimal values reported in the literature as a result of the heating profile associated with this measurement. In effect, by measuring the membranes at 85 °C, the Nafion 117 membranes were ‘heat-treated’, resulting in a decline in conductivity consistent with previous studies or membranes heated beyond 80 °C.[10] Prior to heat treatment before measurement, Nafion 117 membranes had a proton conductivity of 0.099 S/cm when measured in water at 20 °C, (Figure S1) similar to results obtained in literature.[10,33] Since membrane electrode assemblies in fuel cells typically require hot pressing of electrodes onto PEM at temperatures above 100 °C and operate at temperatures above 80 °C wherein fuel cells are more efficient, decline in performance after high temperature treatment in Nafion 117 further reveal that S-tripPEEK membranes are more durable than Nafion 117.

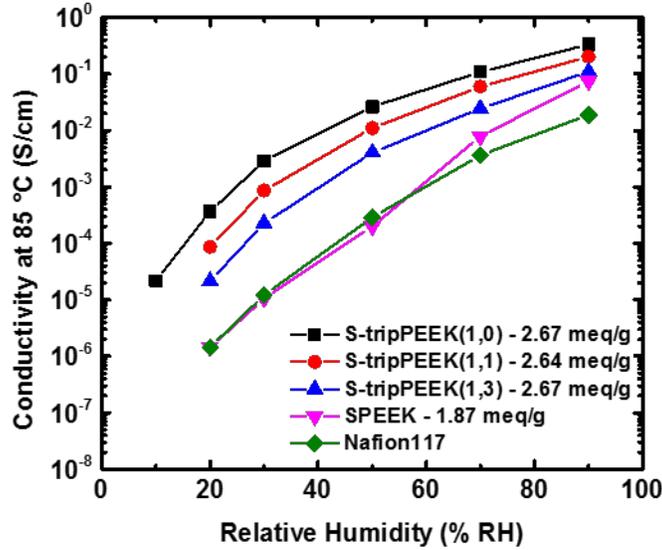


Figure 5. Proton conductivity of membranes 85 °C over different levels of relative humidity.

More importantly, comparing within the S-tripPEEKs membranes clearly reveals that increases in FFV enhances proton conductivities, especially at low relative humidity. Across the full range of relative humidity, S-tripPEEK(1,0) exhibited the highest proton conductivities followed by S-tripPEEK(1,1) and S-tripPEEK(1,3). The enhancement that correlates with FFV varies at different levels of humidity; S-tripPEEK(1,0) has a conductivity 20 times higher than S-tripPEEK(1,3) at 20 %RH but is only 3 times higher at 90 %RH. At low humidity, when the water within the membrane is reduced, the increased free volume in the membrane allowed around 50% more water uptake within the S-tripPEEK(1,0) membrane as compared to S-tripPEEK(1,3) (Table 5) which helps to maintain the hydration number at lower humidity, and hence the enhancement.

Table 5. Water uptake of S-tripPEEK membranes at 20 %RH

	IEC (meq/g)	FFV (cm ³ /cm ³)	Water Uptake (%)	Hydration number, λ
S-tripPEEK (1,0)-2.67	2.67	0.19	9.7	2.02

S-tripPEEK (1,1)-2.64	2.64	0.15	6.6	1.41
S-tripPEEK (1,3)-2.67	2.67	0.11	6.4	1.33

However, at higher humidity, the FFV enhanced water uptake can lead to polymer swelling, which can isolate sulfonates and reduce the conductivity enhancement from FFV. This effect has amplified consequences when the membranes were measured in water at 20 °C. Here S-tripPEEK(1,0) membranes adsorbed water and swelled to such an extent that the sulfonate groups were diluted to the point that the proton conductivity is reduced (Figure 6). As seen in Figure 7, proton conductivities of S-tripPEEK(1,1) were higher than both S-tripPEEK(1,3) and S-tripPEEK(1,0) and is attributed to the larger hydration number observed in S-tripPEEK(1,0). As a side note, S-tripPEEK(1,0) membranes swell by more than 200% in water and are soluble in water at temperatures above 50 °C.

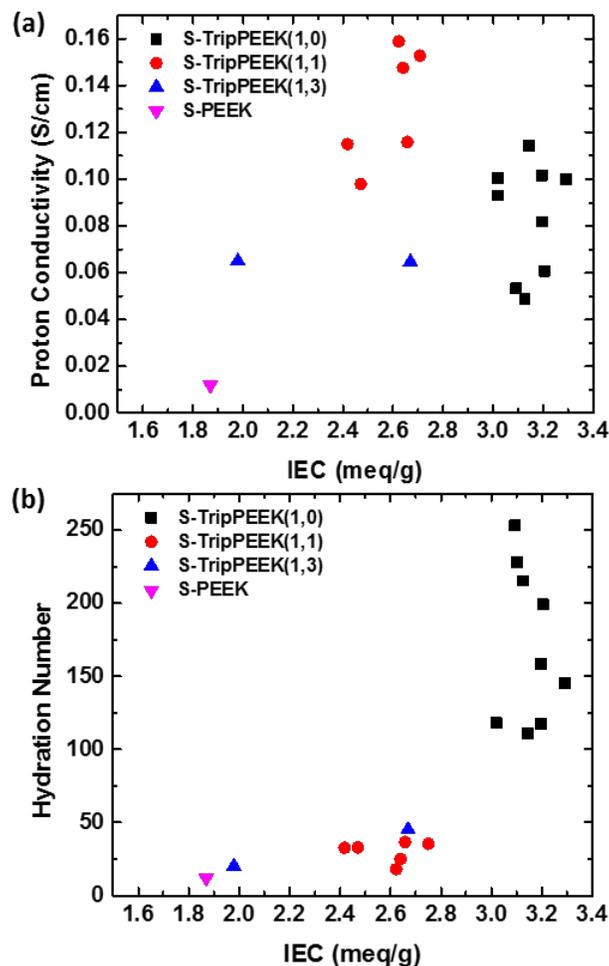


Figure 6. (a) Proton conductivity in water and (b) hydration number of membranes in water. Hydration number is defined as the number of water molecules for every sulfonate group in the membrane.

The dilution of the sulfonates in hydrated S-tripPEEK(1,0) is also consistent with the measured water melting point depressions (Figure 7). Within the membrane, water aggregates around the hydrophilic sulfonate groups, solvating them to release protons. Thus, we can consider the sulfonate groups in the membrane as impurity in the water phase. At a smaller hydration number, there are more sulfonate groups with respect to water molecules in the membrane, resulting in a larger melting point depression of water in the membrane. Hence, with lower

hydration numbers, S-tripPEEK(1,3) and (1,1) shows melting point depressions of -25 to -30 °C while no melting point depression was observed in hydrated S-tripPEEK(1,0) membranes.

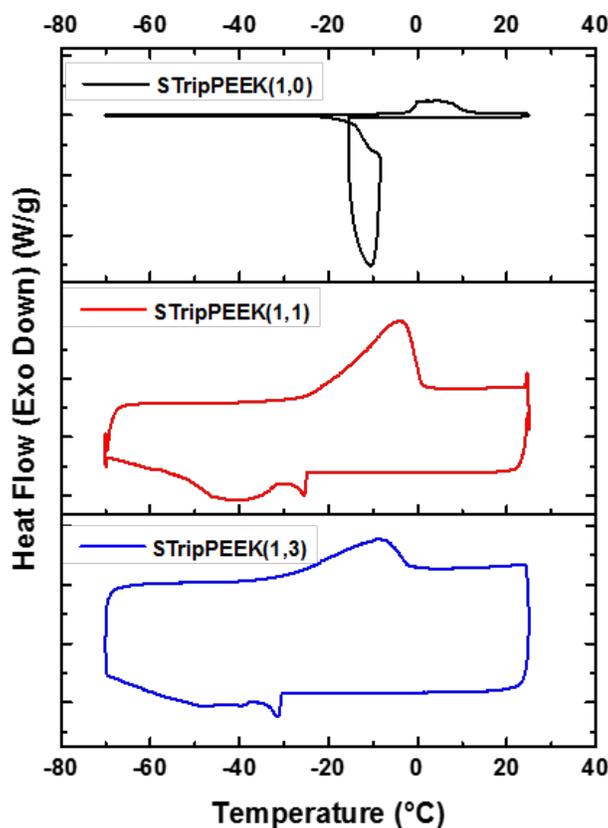


Figure 7. DSC thermograms of hydrated S-tripPEEK films from -70 °C to 25 °C at a heating and cooling rate of 10 °C/min. The loop observed in the cooling cycle of S-tripPEEK(1,0) is due to rapid crystallization of ice. The heat released from the crystallization was higher than the cooling capacity of the instrument and hence raised the temperature of the sample.

To further illustrate the dependence on hydration number and improvements resulting from increasing intrinsic free volume in the membrane, activation energies at different levels of humidity were compared (Figure 8). Activation energies are a measure of the ease of proton transport in the membrane and are highly dependent on water uptake in the membrane. Nafion 117 loses water as the relative humidity decreases with a reduced proton conductivity and increased activation energy. [2,18,34,35] Figure 8 reveals that S-tripPEEKs has a wide window of relative

humidity wherein the activation energies for proton transport were low. More importantly, as the intrinsic free volume increases from S-tripPEEK(1,3) to (1,1) to (1,0), the activation energies decreased across the whole range of humidity. This result suggests that intrinsic free volume enhances the ease of proton transport.

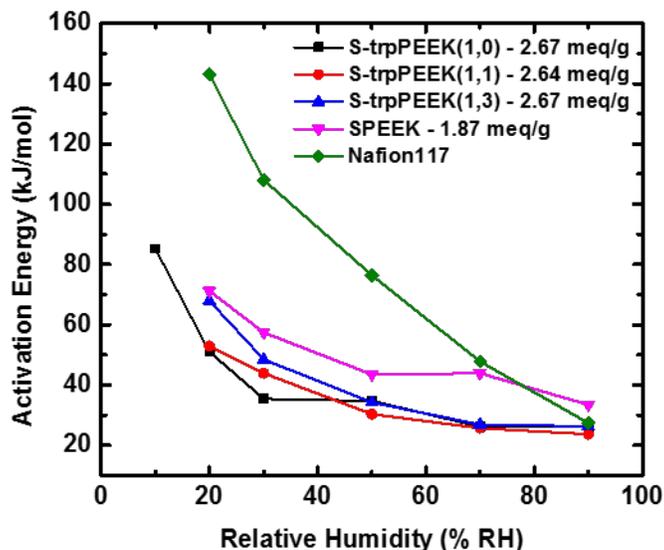


Figure 8. Plot of activation energy observed in each membrane from 20 %RH to 90 %RH. Plots of conductivity vs $1000/T$ used to obtain activation energy plotted in the supplementary information. (Figure S2 – S6)

Conclusion

In summary, a series of proton exchange membranes based on S-tripPEEK with high IEC values and varying levels of intrinsic free volume were synthesized. The membranes exhibit high proton conductivity of 334 mS/cm at 90 %RH and 0.37 mS/cm at 20 %RH at 85 °C, which are much higher than conductivities observed in the commonly used Nafion117 PEMs. Studies of membranes with similar IECs, but increasing intrinsic free volume, at low humidity allowed for successful deconvolution of the effect of free volume from IEC. With increased free volume, water

uptake at low humidity increased, resulting in higher conductivities and a reduction in activation energies for proton conductivity. Considering that PEMFCs should ideally operate at temperatures above the boiling point of water, wherein the humidity is low, intrinsic free volume of PEMFCs should be a major design element.

Acknowledgements

We would like to thank Ms. Sarah Park and Prof. Mircea Dinca at MIT for the use of a humidity chamber, and Mr. Seyed Mirvakili and Prof. Ian Hunter for use of a helium pycnometer which were essential to the work reported here. We would also like to thank the Agency for Science, Technology and Research (Singapore) for a graduate scholarship, the Army Research Office and Institute for Soldier Nanotechnologies for the use of facilities, and Philip Morris International for financial support.

References

- [1] K.A. Mauritz, R.B. Moore, State of Understanding of Nafion, *Chem. Rev.* 104 (2004) 4535–4586. doi:10.1021/cr0207123.
- [2] A. Kusoglu, A.Z. Weber, New Insights into Perfluorinated Sulfonic-Acid Ionomers, *Chem. Rev.* 117 (2017) 987–1104. doi:10.1021/acs.chemrev.6b00159.
- [3] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative Polymer Systems for Proton Exchange Membranes (PEMs), *Chem. Rev.* 104 (2004) 4587–4612. doi:10.1021/cr020711a.
- [4] C. Zhao, G. Zhang, H. Na, Sulfonated Poly(Ether Ketone) Membranes, in: J. Fang, J. Qiao, D.P. Wilkinson, J. Zhang (Eds.), *Electrochem. Polym. Electrolyte Membr.*, CRC Press, 2015: pp. 201–246. doi:10.1201/b18369-6.
- [5] T. Higashihara, M. Ueda, Sulfonated Poly(Ether Sulfone) Membranes, in: J. Fang, J. Qiao, D.P. Wilkinson, J. Zhang (Eds.), *Electrochem. Polym. Electrolyte Membr.*, CRC Press, 2015: pp. 133–200. doi:10.1201/b18369-5.
- [6] J.A. Kerres, Design Concepts for Aromatic Ionomers and Ionomer Membranes to be Applied to Fuel Cells and Electrolysis, *Polym. Rev.* 55 (2015) 273–306. doi:10.1080/15583724.2015.1011754.
- [7] S.J. Peighambari, S. Rowshanzamir, M. Amjadi, Review of the proton exchange membranes for fuel cell applications, *Int. J. Hydrogen Energy.* 35 (2010) 9349–9384. doi:10.1016/j.ijhydene.2010.05.017.
- [8] Y. Zhang, J. Li, L. Ma, W. Cai, H. Cheng, Recent Developments on Alternative Proton Exchange Membranes: Strategies for Systematic Performance Improvement, *Energy Technol.* 3 (2015) 675–691. doi:10.1002/ente.201500028.
- [9] M. Litt, R. Wycisk, Poly(arylenesulfonic acids) with Frozen-In Free Volume as Hydrogen Fuel Cell Membrane Materials, *Polym. Rev.* 55 (2015) 307–329. doi:10.1080/15583724.2015.1023955.
- [10] Y. Sone, Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Impedance Method, *J. Electrochem. Soc.* 143 (1996) 1254. doi:10.1149/1.1836625.
- [11] S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K. Lau, J.H. Lee, Polymer membranes for high temperature proton exchange membrane fuel cell: Recent advances and challenges, *Prog. Polym. Sci.* 36 (2011) 813–843. doi:10.1016/j.progpolymsci.2011.01.003.
- [12] S.S. Araya, F. Zhou, V. Liso, S.L. Sahlin, J.R. Vang, S. Thomas, X. Gao, C. Jeppesen, S.K. Kær, A comprehensive review of PBI-based high temperature PEM fuel cells, *Int. J. Hydrogen Energy.* 41 (2016) 21310–21344. doi:10.1016/j.ijhydene.2016.09.024.
- [13] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Lee, Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs), *Prog. Polym. Sci.* 36 (2011) 1443–1498. doi:10.1016/j.progpolymsci.2011.06.001.
- [14] K.-D. Kreuer, Proton Conductivity: Materials and Applications, *Chem. Mater.* 8 (1996) 610–641. doi:10.1021/cm950192a.
- [15] S.J. Paddison, Proton Conduction Mechanisms at Low Degrees of Hydration in Sulfonic Acid-Based polymer Electrolyte Membranes, *Annu. Rev. Mater. Res.* 33 (2003) 289–319. doi:10.1146/annurev.matsci.33.022702.155102.
- [16] M. Eikerling, A.A. Kornyshev, A.M. Kuznetsov, J. Ulstrup, S. Walbran, Mechanisms of Proton Conductance in Polymer Electrolyte Membranes, *J. Phys. Chem. B.* 105 (2001) 3646–3662. doi:10.1021/jp003182s.

- [17] M.J. Park, S.Y. Kim, Ion transport in sulfonated polymers, *J. Polym. Sci. Part B Polym. Phys.* 51 (2013) 481–493. doi:10.1002/polb.23257.
- [18] G. Blumenthal, M. Cappadonia, M. Lehmann, Investigation of the proton transport in nafion® membranes as a function of direction, temperature and relative humidity, *Ionics (Kiel)*. 2 (1996) 102–106. doi:10.1007/BF02375802.
- [19] K. Sugiyasu, C. Song, T.M. Swager, Tropone-containing polythiophene: synthesis, characterization, and electrochemical properties., *Polym. Prepr. (American Chem. Soc. Div. Polym. Chem.)* 47 (2006) 735–736.
- [20] K. Si, R. Wycisk, D. Dong, K. Cooper, M. Rodgers, P. Brooker, D. Slattery, M. Litt, Rigid-Rod Poly(phenylenesulfonic acid) Proton Exchange Membranes with Cross-Linkable Biphenyl Groups for Fuel Cell Applications, *Macromolecules*. 46 (2013) 422–433. doi:10.1021/ma301875n.
- [21] K. Si, D. Dong, R. Wycisk, M. Litt, Synthesis and characterization of poly(para-phenylene disulfonic acid), its copolymers and their n-alkylbenzene grafts as proton exchange membranes: high conductivity at low relative humidity, *J. Mater. Chem.* 22 (2012) 20907. doi:10.1039/c2jm33066k.
- [22] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: A review, *Polymer (Guildf)*. 54 (2013) 4729–4761. doi:10.1016/j.polymer.2013.05.075.
- [23] K. Miyatake, Y. Chikashige, E. Higuchi, M. Watanabe, Tuned Polymer Electrolyte Membranes Based on Aromatic Polyethers for Fuel Cell Applications, *J. Am. Chem. Soc.* 129 (2007) 3879–3887. doi:10.1021/ja0672526.
- [24] H.-F. Lee, Y.-C. Huang, P.-H. Wang, C.C. Lee, Y.-S. Hung, R. Gopal, S. Holdcroft, W.-Y. Huang, Synthesis of highly sulfonated polyarylene ethers containing alternating aromatic units, *Mater. Today Commun.* 3 (2015) 114–121. doi:10.1016/j.mtcomm.2015.01.006.
- [25] F. Gong, S. Zhang, Synthesis of poly(arylene ether sulfone)s with locally and densely sulfonated pentyptycene pendants as highly conductive polymer electrolyte membranes, *J. Power Sources*. 196 (2011) 9876–9883. doi:10.1016/j.jpowsour.2011.08.028.
- [26] F. Gong, H. Mao, Y. Zhang, S. Zhang, W. Xing, Synthesis of highly sulfonated poly(arylene ether sulfone)s with sulfonated triptycene pendants for proton exchange membranes, *Polymer (Guildf)*. 52 (2011) 1738–1747. doi:10.1016/j.polymer.2011.02.033.
- [27] S.A. Sydlik, Z. Chen, T.M. Swager, Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices, *Macromolecules*. 44 (2011) 976–980. doi:10.1021/ma101333p.
- [28] J.P. Amara, T.M. Swager, Incorporation of Internal Free Volume: Synthesis and Characterization of Iptycene-Elaborated Poly(butadiene)s, *Macromolecules*. 37 (2004) 3068–3070. doi:10.1021/ma0354694.
- [29] T.M. Swager, Iptycenes in the design of high performance polymers., *Acc. Chem. Res.* 41 (2008) 1181–9. doi:10.1021/ar800107v.
- [30] P.D. Bartlett, M.J. Ryan, S.G. Cohen, Triptycene 1 (9,10-o-Benzoanthracene), *J. Am. Chem. Soc.* 64 (1942) 2649–2653. doi:10.1021/ja01263a035.
- [31] Z. Xie, C. Song, B. Andreaus, T. Navessin, Z. Shi, J. Zhang, S. Holdcroft, Discrepancies in the Measurement of Ionic Conductivity of PEMs Using Two- and Four-Probe AC Impedance Spectroscopy, *J. Electrochem. Soc.* 153 (2006) E173. doi:10.1149/1.2258091.
- [32] Y. Shao, G. Yin, Z. Wang, Y. Gao, Proton exchange membrane fuel cell from low

- temperature to high temperature: Material challenges, *J. Power Sources*. 167 (2007) 235–242. doi:10.1016/j.jpowsour.2007.02.065.
- [33] T.A. Zawodzinski, Water Uptake by and Transport Through Nafion® 117 Membranes, *J. Electrochem. Soc.* 140 (1993) 1041. doi:10.1149/1.2056194.
- [34] Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda, Depression of proton conductivity in recast Nafion® film measured on flat substrate, 2009. doi:10.1016/j.jpowsour.2008.12.141.
- [35] M. Cappadonia, Conductance of Nafion 117 membranes as a function of temperature and water content, *Solid State Ionics*. 77 (1995) 65–69. doi:10.1016/0167-2738(94)00289-5.

For table of contents use only

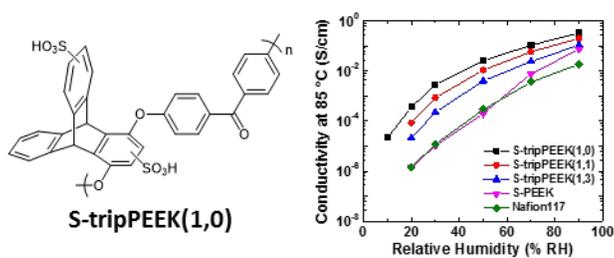
Free Volume Enhanced Proton Exchange Membranes from Sulfonated Triptycene Poly(Ether Ether Ketone)

Lionel C.H. Moh, John B. Goods, Timothy M. Swager*

Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Abstract

Triptycene based poly(ether ether ketone) (tripPEEK) were synthesized and sulfonated to form proton exchange membranes. The increase in intrinsic free volume resulting from the incorporation of sterically bulky triptycene moiety, imparts high affinity to water at all levels of relative humidity (RH) from 10 %RH to 90 %RH. S-tripPEEK membranes showed proton conductivities of 334 mS/cm at 85 °C at 90 %RH and 0.37 mS/cm at 85 °C at 20 %RH as compared to 18.9 mS/cm and 0.0014 mS/cm observed in Nafion17™ membranes measured under the same respective conditions. Membranes of similar ion exchange capacity (IEC) are also compared to deconvolute the effect of free volume from IEC in enhancing proton conductivity. Increasing the free volume of the membranes increases the proton conductivity and decreases the activation energy for proton conduction at low humidity.



TOC Figure