

SPEEK/functionalized silica composite membranes for polymer electrolyte fuel cells

Satheesh Sambandam, Vijay Ramani*

Center for Electrochemical Science and Engineering, Department of Chemical and Environmental Engineering, Illinois Institute of Technology, Chicago, IL 60616, USA

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Abstract

Silica and sulfonic acid functionalized silica were synthesized by condensation of appropriate precursors through a sol–gel approach. SPEEK with three different ion exchange capacities (1.35, 1.75 and 2.1 mequiv. g⁻¹) were prepared by sulfonation of PEEK. Composite membranes with 5% and 10% additive loadings were prepared by solvent casting. Characterization by FTIR spectroscopy confirmed the presence of sulfonic acid groups in the functionalized silica additives. The agglomerate size of the additives was estimated by scanning electron microscopy to be between 2 and 5 μm. The room temperature liquid water uptake of the membranes was evaluated. Water uptake increased with SPEEK IEC. Composite membranes exhibited lower water uptakes when compared to pure SPEEK. Proton conductivities of up to 0.05 S cm⁻¹ at 80 °C and 75% relative humidity and 0.02 S cm⁻¹ at 80 °C and 50% relative humidity were recorded for SPEEK composite membranes prepared using sulfonic acid functionalized silica. Hydrogen crossover through the membrane was determined through linear sweep voltammetry on membrane electrode assemblies (MEAs). Hydrogen crossover current densities for all the MEAs were on the order of 1–2 mA cm⁻². MEAs tested showed reasonable performance at 80 °C and 75% and 50% relative humidities.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have been widely researched in recent years as they have potential applications in transportation, stationary power, portable power and military use. There remain several challenges, both technical and economical, that need to be overcome prior to fuel cell commercialization. Two of the major hurdles are cost and performance. Hence, widespread research is being carried out to find alternate membrane and catalyst materials that are less expensive but exhibit performance equivalent or superior to the state of the art.

1.1. Current materials for polymer electrolyte membranes

The membrane electrode assembly (MEA) is an integral part of the PEM fuel cell. It consists of a proton conducting PEM that

is sandwiched between two catalyst layers (usually platinum or platinum alloys supported on carbon) that serve as electrodes. PEMs in general have a functional group (usually sulfonic acid) attached to the polymer backbone. This group facilitates proton conduction. Upon hydration, the PEMs tend to show an increase in the proton conductivity. Some of the most promising PEMs are Nafion[®] (Dupont), Flemion[®] (Asahi Glass company), Aciplex[®] (Asahi chemical Industry), Neosepta-F[®] (Tokuyama) and Gore-Select[®] (W.L. Gore and Associates) [1]. Although some of these membranes were originally developed for chlor-alkali electrolysis, they demonstrate good proton conductivities when used as electrolytes in a PEM fuel cell. Some of the requirements of PEMs, apart from high proton conductivity, include good chemical, morphological and thermal stability; excellent chemical durability; and low cost. Current limitations in PEMs are poor proton conductivity at elevated temperatures (>100 °C) and low humidities; susceptibility to chemical degradation; and high cost. In addition to the above problems, most membranes also show high methanol crossover, which is detrimental to operation in direct methanol mode. Hence development of alternate membranes with desirable properties has been widely explored.

* Corresponding author. Tel.: +1 312 567 3064; fax: +1 312 567 8874.
E-mail address: ramani@iit.edu (V. Ramani).

Hydrocarbon membranes look promising in this scenario though durability remains a concern. Some of the hydrocarbon polymers studied include poly(styrene sulfonic acid), sulfonated poly(ether ether ketone) [2], sulfonated poly(ether sulfone) [3], sulfoarylated polybenzimidazole [4,5], sulfonated polyimides [6], sulfonated poly(phenylene sulfide) and sulfonated poly(phenoxy benzoyl phenylene).

1.2. Inorganic additives

Protons conducting additives like silica, zirconium phosphate [7–9], heteropolyacids (HPAs) [10–13] and various metal oxides have also been added to PEMs. They are usually hygroscopic and proton conducting by themselves or with help of attached acidic moieties. Various research groups have tried to improve the ionic conductivity of Nafion[®] at elevated temperatures [14–16]. Watanabe et al. [17] first presented their work on the use of hygroscopic oxides for perfluorosulfonic acid membranes. Following that, sol–gel derived silica was used as an additive to Nafion[®] [18,19]. Nafion[®] solution was later used with slight modification in the sol–gel process to prepare homogenous silica–Nafion[®] composite membranes [20]. Bonnet et al. [2] studied the properties of sulfonated poly(ether ether ketone) based hybrid membranes comprising particles of amorphous silica, sulfophenyl phosphate, and zirconium phosphate as a function of temperature and humidity. An important effect that results on addition of these additives is reduced methanol permeability. This greatly augments the performance in direct methanol mode. For example, Stangar et al. [21] showed that silica functionalized with poly(propylene glycol) and doped with a heteropolyacid showed better results than Nafion[®] in a direct methanol fuel cell (DMFC). Membranes based on hydrocarbon polymers with oxo-acids have also been shown to give high conductivity at elevated temperatures $\sim 160^\circ\text{C}$ [22,23]. H_3PO_4 has been added as an additive to poly(benzimidazole) and poly(benzimidazole) blends to yield high temperature membranes [24,25]. Finally, to address the issue of membrane durability, Konishi et al. [26] claims that proton conducting polymer electrolytes based on poly(ether sulfone) with protons of the sulfonic acid groups in their polymers partly exchanged by metal ions such as magnesium, titanium, aluminium, and lanthanum ions demonstrated improved durability. This can serve as a positive approach to enhance durability of hydrocarbon membranes.

1.3. PEEK

Poly(ether ether ketone) (PEEK) is an aromatic, semi-crystalline polymer which shows mild solubility in organic solvents due to its crystallinity. By sulfonating PEEK, crystallinity is decreased and solubility is increased [27,28]. This makes membrane dissolution (and casting) easier using organic solvents like dimethyl acetamide (DMAc)/dimethyl formamide (DMF). It has been observed that when DMAc/DMF is used, the membranes possess an amorphous structure and the chemical and physical properties are similar to that of sulfonated polymer [29]. The sulfonation reaction involving PEEK can be

well controlled by reaction time, temperature and concentration of sulfuric acid. Kreuer [30] inferred from small angle X-ray scattering (SAXS) experiments that hydrophilic/hydrophobic difference is lower and flexibility of the polymer backbone is smaller in poly(ether ketones). Therefore the separation into hydrophilic and hydrophobic domains is less pronounced when compared to Nafion[®]. This leads to narrower channels in sulfonated poly(ether ketones) and hence lowers electro-osmotic drag for given water content. Good thermal stability of these polymer membranes should allow us to operate the fuel cell at elevated temperatures (100–120 °C).

SPEEK has been reported in the literature as a low cost alternate membrane for both PEMFC and DMFC applications [31,32]. Xue and Yin [33] reported methanol permeability and selectivity for SPEEK membranes of different degrees of sulfonation. According to their results, SPEEK had lower methanol permeability and higher selectivity than Nafion[®] 117. Jiang et al. [34] and Yang and Manthiram [35] used multilayer SPEEK membranes for DMFCs to reduce methanol crossover. Since cross linking is thought to be an effective approach to reduce water swelling and methanol crossover, Zhong et al. [36] and Zhao et al. [37] recently cross linked SPEEK by direct copolymerization of sulfonated monomers.

1.4. SPEEK composite membranes

There are several justifications for the development of composite membranes: (1) to prevent membrane (anode side) dry out by addition of hydrophilic materials, (2) to suppress the methanol crossover, (3) to better withstand mechanical stress during swelling–deswelling phenomena, and (4) to increase the pathways of proton conduction.

Extensive work has been made till date to develop inorganic-organic composite SPEEK membranes. This includes use of zirconium phosphate, boron phosphate [38], tungsten oxides [39], silica, silica supported zirconium phosphate and heteropolyacids [40] as additives to SPEEK. Mikhailenko et al. [38] observed a conductivity of 0.05 S cm^{-1} at 160°C and fully hydrated conditions while Zaidi et al. [40] reported 0.1 S cm^{-1} above 100°C with thermal stability up to temperatures above 250°C in SPEEK/HPA membranes. Though membranes loaded with HPAs showed high water uptake and good proton conductivity, the HPAs tend to dissolve in water present in the membrane due to its high solubility. To avoid dissolution, HPAs were loaded onto MCM-41 (mesoporous silica) [41]. Alberti and Casciola [7] thoroughly investigated zirconium phosphate sulfophenylphosphonate Zr(SPP) [2], and Krishnan et al. [42] reported a threefold increase in the conductivity of SPEEK with 50% loading of Zr(SPP). Krishnan et al. [43] also introduced Boron phosphate, prepared by an in situ sol–gel process, to SPEEK and showed almost sixfold increase in the conductivity when compared to pure SPEEK membranes. Licoccia et al. [44] prepared a modified silane bearing sulfonic acid functionality (sulfonated diphenylsilanediol, SDPSD) and made a SPEEK composite membrane with promising conductivity at 120°C . Nunes et al. [45] claimed a remarkable reduction of the methanol and water permeability by inorganic modification of

SPEEK by in situ hydrolysis of different alkoxides of Si, Ti and Zr.

1.5. Current work

The concept of composite membranes for fuel cells thus first started with Nafion[®] and later extended to hydrocarbon membranes for both PEFCs and DMFCs. In this study we have explored the use of silica functionalized with sulfonic acid. These additives were prepared by a modified sol–gel route by co-condensation of organo-silane precursors [46]. SPEEK/functionalized silica composite membranes were tested to determine the proton conductivity and PEFC performance. The precursor used for sulfonic acid functionalized silica synthesis was 3-mercaptopropyltrimethoxy silane (MPTMS). The surfactant free synthesis of functionalized silica from MPTMS was first demonstrated by Johnston et al. [47] for applications in bio-molecular screening. The thiol functionalized silica obtained can be converted to sulfonic acid functionalized silica by oxidation. Non-functionalized silica particles were also prepared as part of the current study. The best known process for synthesis of silica particles is the Stober's process [48]. There have been many reports of modifications to the original Stober's process by the use of different catalysts. The process is either acid or base catalyzed. In this study, silica was prepared by acid catalyzed sol–gel route from tetra ethylortho silicate (TEOS) precursor [49]. To the best of our knowledge, this is the first report on SPEEK/functionalized silica system in an operating fuel cell. The conductivity of sulfonic acid functionalized mesostructured porous silica was first reported by Mikhailenko et al. [50]. Later Hamoudi and Kaliaguine [51] incorporated sulfonic acid groups in silica without collapsing the structure and showed that these sulfonic acid anchored materials were thermally stable until 200 °C. While this work was in progress, there have been two reports on sulfonic acid functionalized silica/Nafion[®] composites [52,53].

2. Experimental

2.1. SPEEK synthesis

Ten grams of PEEK powder was dried in the oven at 80 °C prior to sulfonation. The powder was then added to 200 cm³ of concentrated sulfuric acid (H₂SO₄, 95–98% ACS) very slowly, with continuous stirring on a stirrer plate. Care was taken to prevent formation of lumps as they result in non-uniform sulfonation of PEEK. After addition of PEEK, the conical flask was covered with parafilm to prevent contact with moisture in the air. After the desired amount of sulfonation, the sulfonated polymer (SPEEK) was precipitated out by pouring the solution in deionized water through a funnel with a fine bore, yielding thin strands of SPEEK. Thin strands were easier to wash due to better mass transfer (faster removal of sulfuric acid). The SPEEK strands were washed thoroughly to remove excess acid until the pH of the wash solution was ~6 and then dried at room temperature. The extent of sulfonation was controlled by the reaction time and was measured by calculating ion exchange capacity (IEC).

IEC is defined as milliequivalents of H⁺ per gram of ionomer. In this work three different samples of SPEEK with different sulfonation levels (hence three IECs) corresponding to reaction times of 72, 120 and 168 h were obtained.

2.2. Determination of IEC

SPEEK samples (~300 mg) of three different sulfonation levels were dried at 110 °C and their dry weight was noted. They were then immersed in a known quantity of 0.1 M NaCl solution for 24 h with stirring. Protons in the sulfonic acid group exchanged with the sodium ions in solution. A known volume of the solution was taken and titrated against 0.1 M NaOH using phenolphthalein indicator to quantify the amount of protons in the solution. From this information and the weight of the polymer, the IEC was estimated.

2.3. Synthesis of silica additives

Two different silica additives were prepared: (1) a non-functionalized additive with TEOS (tetraethylorthosilicate, 99.999%, Aldrich) as precursor, and (2) a sulfonic acid functionalized with MPTMS (3-mercaptopropyltrimethoxy silane, 95%, Aldrich) as precursor. Ethanol was added to a solution of TEOS, followed by water and HCl (37% by weight) in the mole ratio TEOS:H₂O:ethanol:HCl; 1:30:10:6. HCl was the catalyst for the reaction. The contents of the mixture were well stirred for 1 h and kept in an oven at 60 °C for 24 h to form a gel. Once dried, the gel was crushed using a mortar and pestle to form fine white powders of silica.

Functionalized silica particles from MPTMS were prepared using the procedure given in the literature [46]. 0.44 mol of water was taken in a vial and the solution was acidified by adding 0.16 cm³ of 0.1 M HCl. To this mixture 5.38 mmol of MPTMS was added and the whole solution stirred for 18 h. 6 μL of NH₄OH was added and after 30 min the sample was centrifuged and washed thoroughly to remove any unreacted MPTMS using ethanol. The particles obtained were dried overnight at 50 °C. The silica particles thus produced had thiol groups attached on the surface which need to be oxidized to sulfonic acid group by adding peroxide. A detailed description of this reaction mechanism along with the reaction scheme can be found elsewhere [47]. The thiol functionalized silica particles were then dispersed in excess peroxide solution (35 wt%, Sigma–Aldrich) for 3–4 h to convert thiol to sulfonic acid. Finally, the sulfonic acid functionalized silica was dried at 50 °C.

2.4. Fourier transform-infra red spectroscopy (FTIR)

FTIR spectra for the prepared silica and functionalized silica particles were recorded [Nicolet-100, Thermo Electron] in the frequency range 4000–400 cm⁻¹ for comparing positions of the IR bands and to check for the presence of functional groups on the silica surface. The recorded spectrum was an average of 64 scans in the transmittance mode using samples embedded in dry KBr pellets.

2.5. Scanning electron microscopy (SEM)

Silica and functionalized silica additives were characterized by SEM (Model S-3000N, Hitachi) to estimate their particle sizes. From the SEM images, the mean particle/agglomerate sizes of the two additives were estimated.

2.6. Membrane preparation

450 mg of SPEEK sample was dissolved in 8–10 cm³ of DMAc. Membranes were prepared by casting the appropriate precursor solution on a 7.5 cm × 7.5 cm glass plate, followed by overnight drying at 60 °C for solvent evaporation. The membranes were then peeled off from the glass plate and the edges were cut and discarded. Finally the membranes were hot-pressed at 120–130 °C and 2.75 MPa for 5 min. Composite membranes were prepared by addition of silica and functionalized silica additives to the SPEEK/solvent mixture to form membranes with two additive loadings (5 and 10 wt%).

2.7. Liquid water uptake

Membranes samples of area approximately 3 cm × 3 cm were dried at 110 °C for 4 h to bring each sample to an identical starting state. The membrane samples were then weighed to note the dry weight. The samples were then immersed in deionized water for 24 h for the water uptake. The membranes were removed from water, blotted to remove any water on the surface before weighing. From the final weight, the percentage water uptake can be calculated as:

%water uptake =

$$\frac{\text{Weight after water uptake} - \text{Dry weight}}{\text{Dry weight}} \times 100$$

2.8. MEA preparation

SPEEK membranes with IEC-1.75 mequiv. g⁻¹ composite membranes with 10 wt% additive loadings were used for MEA preparation. To prepare catalyst ink, 40 wt% platinum supported on carbon (Alfa Aesar) was taken in a glass vial and deionized water was added drop-wise to wet the surface. Methanol and Nafion[®] 1100 (5% dispersion) were added to make an ink with 30 wt% ionomer loading (with respect to total catalyst weight). The catalyst ink was then stirred for 4–6 h for good dispersion. MEAs were prepared by spraying ink onto the membrane using a spray gun. A heating lamp was placed behind the membrane to evaporate the solvent as ink was sprayed onto the membrane surface. All prepared MEAs were of 5 cm² active area, with a catalyst loading of 0.4 mg cm⁻² on cathode side and 0.2 mg cm⁻² on the anode side. The MEAs were hot pressed at 120–130 °C for 5 min at 2.75 MPa.

The MEAs were assembled in a 5 cm² fuel cell hardware containing serpentine flow fields. Commercial carbon paper gas diffusion layers (SGL Carbon) and PTFE gaskets were used. A pinch (defined as the difference between the sum of the thick-

nesses of the MEA and GDLs and the total thickness of gaskets used) of 330 μm was used during cell assembly. The fuel cell hardware was assembled by applying a uniform torque of 3.0 Nm to each of eight bolts in three increments.

2.9. LSV and CV

Linear sweep voltammetry was the first experiment performed on each cell to check for hydrogen crossover and electronic shorting in the MEA. H₂ was passed through the anode side at a flow rate of 0.2 slpm, while N₂ was passed through the cathode side at the same flow rate. Both gases were saturated at room temperature (25 °C). The working electrode (cathode) was swept from 0 to 0.8 V (versus SHE) at 4 mV s⁻¹ and the current due to oxidation of crossover hydrogen was recorded. The flux of hydrogen crossover was estimated from the value of the limiting current obtained in the voltammogram using Faraday's law. Cyclic voltammetry experiments were performed to ensure catalyst surface was active. A scan rate of 30 mV s⁻¹ was used to sweep the working electrode from 0 to 0.8 V (versus SHE) and back.

2.10. Resistance and conductivity measurement

The membrane resistance was measured using the current interrupt technique built into the fuel cell test station (Model 850 C, Scribner Associates). The Fuel Cell[®] software was used to record the resistance, voltage, current, temperature and gas flow rates simultaneously. The resistance was measured at 80 °C and two inlet relative humidities: 75% and 50%. The relative humidities were controlled by controlling the dew points of the reactant gas saturators built into the test station. Typically, after equilibrating with hydrogen on the anode and oxygen on the cathode, the resistance value was invariant with time and was noted at a constant current of 2 A (400 mA cm⁻²) for 75% RH and 1 A (200 mA cm⁻²) for 50% RH for each MEA. From the membrane thickness and area (5 cm²), through-plane conductivity was calculated from the measured resistance as follows:

$$\text{Conductivity (S cm}^{-1}\text{)} = \frac{\text{Thickness (cm)}}{\text{Resistance (}\Omega\text{)} \times \text{Area (cm}^2\text{)}}$$

2.11. MEA performance testing

The performance of the MEAs were evaluated at 80 °C and inlet relative humidities of 75% (corresponding to a saturator dew point of 73 °C) and 50% (corresponding to a saturator dew point of 64 °C). Air was used as oxidant (cathode flow rate = 0.2 slpm) and pure hydrogen was used as fuel (anode flow rate = 0.2 slpm). While starting up the cell, care was taken to prevent any condensation inside the cell by always maintaining the cell and line temperatures higher than the saturator temperature. Before running a polarization curve for a given set of operating conditions, the MEA was allowed to equilibrate for a minimum of 45 min. In a typical polarization experiment the voltage was scanned from the open circuit voltage (OCV) down to at least 0.4 V.

3. Results and discussion

PEEK [poly(oxy-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene)] is a chemically and thermally stable aromatic polymer [1] that can be sulfonated by concentrated sulfuric acid [54] or chlorosulfonic acid [55]. Since sulfonation by fuming sulfuric acid or chlorosulfonic acid may also lead to chemical degradation, concentrated sulfuric acid is the most preferred chemical agent for PEEK sulfonation reaction and was used in this study.

As reported by Jin et al. [54], sulfonation of each PEEK unit takes place in the phenylene ring flanked by ether groups. During the sulfonation reaction, only one of the four protons in the ring is being substituted by the sulfuric acid, even though there are four ortho positions for sulfonation. Due to the electron withdrawing effect of carbonyl group in the PEEK repeating unit, the other two phenyl rings attached to the carbonyl group are not favored for the electrophilic sulfonation. Since the sulfonic acid group is also electron withdrawing, further sulfonation on the same phenyl ring does not occur. This electrophilic substitution reaction is assumed to be second order with respect to the aromatic ring concentration and the reverse reaction is neglected under the conditions of high acid concentrations [56]. The rate of the sulfonation reaction decreases with time: (i) due to the consumption of PEEK and (ii) decrease in the concentration of sulfuric acid due to the formation of water as a by-product. The effect of the latter is considered to be negligible due to insignificant change in the acid concentration [57]. Sulfonic acid group cross-linking is not observed during the reaction at room temperature with 98% H_2SO_4 [58]. Thus, PEEK with sulfonic acid group ($-\text{SO}_3\text{H}$) shows properties of an ionic conductor.

The extent of sulfonation of PEEK is usually reported by quantifying the sulfonic acid groups in the polymer chain. This can be done by measuring sulfonation degree (SD) or ion exchange capacity (IEC) of SPEEK. The SD is the mole ratio of sulfonated PEEK units to that of total PEEK units. SD can be determined by ^1H NMR as described in Nolte et al. [59] or from the IEC values [60]. In this study, only the IEC was determined.

3.1. Ion exchange capacity

The following nomenclature will henceforth be used for denoting SPEEK of different IECs: the sulfonation time (in days) will follow SPEEK to distinguish one from the other—i.e. the sample with 120 h of sulfonation will be referred to as SPEEK-5. Fig. 1 shows the plot of SPEEK IEC as a function of reaction time.

The IEC of SPEEK shows an increasing trend with reaction time due to the presence of more repeating units of PEEK with sulfonic acid group in the polymer chain. The maximum IEC of the prepared SPEEK samples is 2.1 mequiv. g^{-1} corresponding to a reaction time of 7 days while the least is 1.35 mequiv. g^{-1} , corresponding to a reaction time of 3 days. Even the latter value is higher than the IEC of Nafion[®] 1100 (0.9 mequiv. g^{-1}). The reported value of each IEC is an average of at least three values and the error associated with the measurement (standard error) is indicated by the error bars.

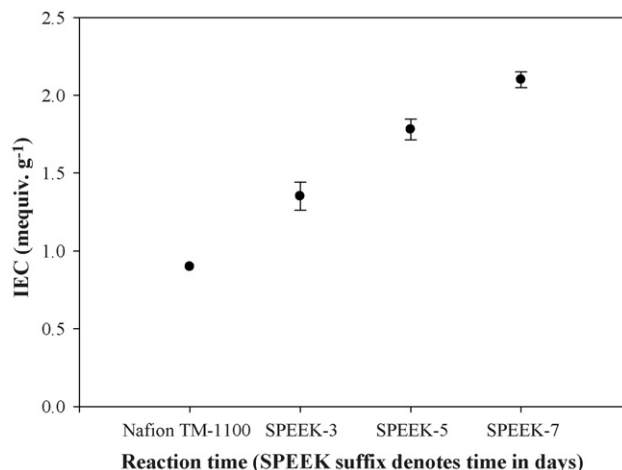


Fig. 1. Variation of IEC of SPEEK with reaction time.

3.2. Liquid water uptake

Fig. 2 is a plot of percentage liquid water uptake for SPEEK and different SPEEK composite membranes calculated based on the dry weight of the membrane. Sulfonation of polymers has a significant impact on water uptake, which in turn determines proton conductivity and mechanical properties of the membrane.

The plot is divided into three regions corresponding to membranes prepared using different SPEEK IECs. Region I corresponds to SPEEK-3 (IEC = 1.35 mequiv. g^{-1}), region II to SPEEK-5 (IEC = 1.75 mequiv. g^{-1}) and region III to SPEEK-7 (IEC = 2.1 mequiv. g^{-1}). There are two distinct observations that can be made from the plot: (1) water uptake for pure SPEEK membranes and composite SPEEK membranes increase with IEC; (2) the SPEEK composite membranes exhibit lower liquid water uptake when compared to pure SPEEK although

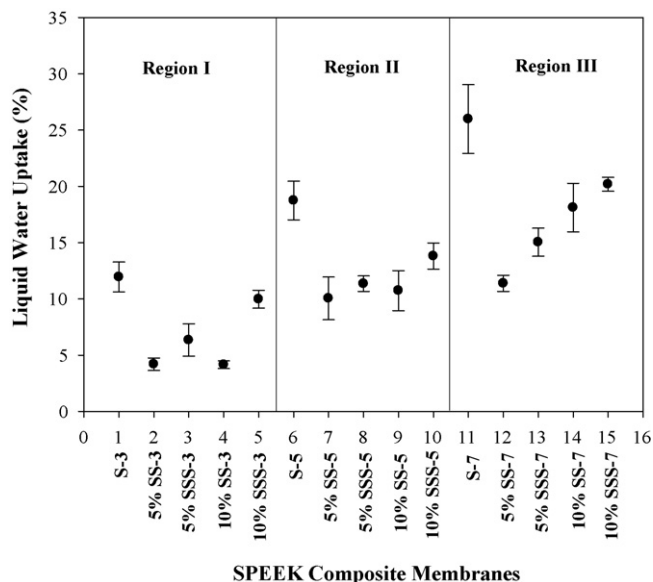


Fig. 2. Room temperature liquid water uptake for different SPEEK and composite SPEEK membranes; S: SPEEK; SS: silica/SPEEK composite membrane; SSS: sulfonic acid functionalized silica/SPEEK composite membrane; prefix denotes additive loadings and suffix denotes PEEK sulfonation time in days.

the additives are hydrophilic in nature. The first observation is attributed to the increase in the number of hydrophilic sulfonic acid groups attached to the polymer chain. The second observation is primarily attributed to the lowering in swelling due to the presence of the additive particles [65]. A secondary reason for this phenomenon is the ability of the additives to hold on to water molecules even at elevated temperatures [63–65]. Hence, the baseline dry weight for these membranes will be higher as it includes water bound to the additive within the membrane. For each IEC, the SPEEK membranes with sulfonic acid functionalized silica showed higher water uptakes when compared to the SPEEK membranes with non-functionalized silica. The low surface to volume ratio of these particles (discussed in Section 3.4) was responsible for limiting the enhancement in water uptake despite the presence of hydrophilic sulfonic acid groups on the surface of functionalized silica. Increasing the loading of silica from 5 to 10 wt% did not change the measured liquid water uptake for SPEEK-3 and SPEEK-5 based membranes. However, an anomalous increase was seen in the case of SPEEK-7 based membranes. In the case of sulfonic acid functionalized silica, the liquid water uptake did increase when the additive loading was increased from 5 to 10 wt%. This increase was expected as the number of hydrophilic sulfonic acid groups introduced along with the functionalized silica also increased.

3.3. FTIR

FTIR spectra of sol-gel derived silica and functional silica were recorded and shown in Fig. 3. The broadband in between 3600 and 3200 cm^{-1} corresponds to the O–H stretching of the silanol groups. The intense band at 1100–1000 cm^{-1} indicates siloxane stretching in all the silica samples, which includes the band at 1030 cm^{-1} for –Si–O–Si– linear stretching and the band at 1080 cm^{-1} for –Si–O–Si– cyclic stretching. In addition –Si–O–Si– asymmetric stretching can be observed at 810 cm^{-1} [15]. Angular vibration of water molecule can also be observed at 1650 cm^{-1} [61]. The attachment of organic molecule on the

silica surface is usually confirmed by a weak band at 2950 cm^{-1} , which is not seen here due to weak signal. Bending vibrations of Si–O can also be observed in all samples at 470 cm^{-1} . More importantly the band at 2575 cm^{-1} for thiol vibrations in functionalized silica derived from MPTMS disappears upon oxidation. Simultaneously, a band corresponding to sulfonic acid group at 1050 cm^{-1} [62] appears in the spectrum of the oxidized functionalized silica. In addition, a band at 1200 cm^{-1} in the spectra of functionalized silica spectra indicates $-\text{SO}_3^-$ asymmetric stretching [15] which further confirms the attachment of sulfonic acid on to the silica network.

3.4. SEM

Fig. 4a and b are SEM images of silica and sulfonic acid functionalized silica particles, respectively. The particle/agglomerate size of both silica and sulfonic acid functionalized silica range from sub-micron particles to agglomerates of 2–5 μm . The 2–5 μm agglomerates predominate in the membrane, and hence the sizes of the inorganic domains are similar to one another in the composite membrane and permit direct comparison. The surface to volume ratio was estimated for an agglomerate size range of 2–5 μm . For a spherical particle/agglomerate of diameter

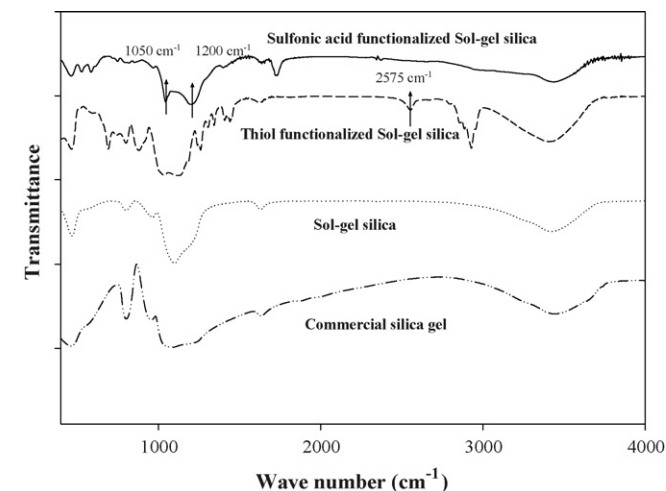


Fig. 3. FTIR spectra of silica and functionalized silica particles with KBr.

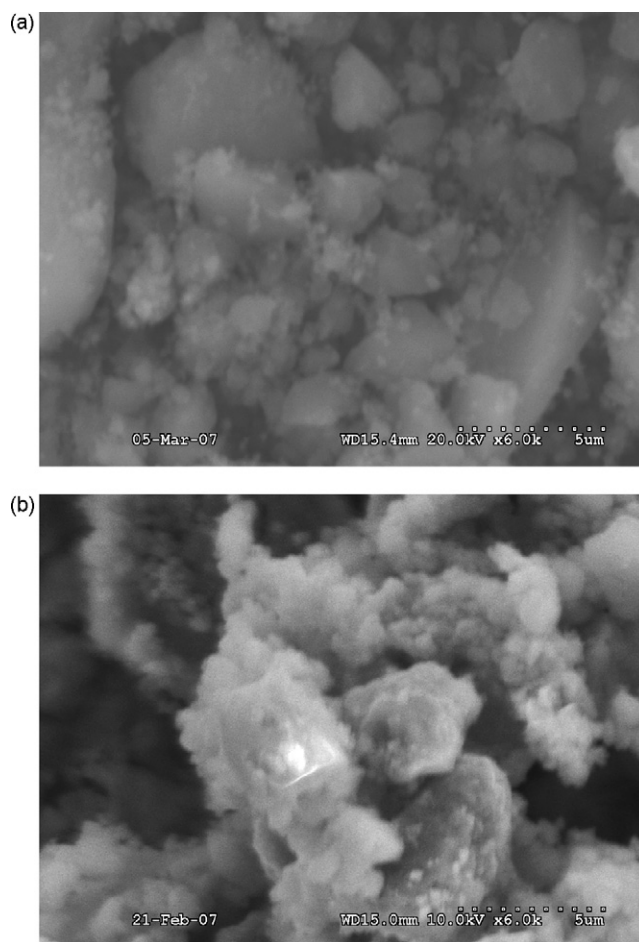


Fig. 4. (a) SEM image of sol-gel derived silica particles. (b) SEM image of sulfonic acid functionalized silica particles.

2 μm , the surface to volume ratio is $30,000 \text{ cm}^2 \text{ cm}^{-3}$. Surface to volume ratio is an inverse function of particle diameter and hence a diameter of 5 μm will have a surface to volume ratio $12,000 \text{ cm}^{-1}$. This is the range of surface to volume ratios that the additives in the composite membranes exhibit. These numbers are relatively low (large agglomerate size) and hence result in only a fraction of the sulfonic acid functionality in the functionalized additive being effective (on the surface) and contributing to water uptake and conductivity.

3.5. Linear sweep voltammetry

LSV was the first experiment performed on each MEA and was also performed on each MEA after completion of testing. The current associated with the oxidation of hydrogen crossing over through the membrane was recorded by LSV. The measured current is a direct measure of hydrogen crossover flux and was used as an estimate to check if the membranes were robust without any holes. Hydrogen crossover current densities for all the MEAs were on the order of $1\text{--}2 \text{ mA cm}^{-2}$. The absence of significant slope in the limiting current region for all the three membranes (before and after testing) indicated the absence of internal shorting in any of the MEAs. The resistance values determined by the current interrupt technique are therefore reliable estimates of the membrane resistance.

3.6. Conductivity

SPEEK-3 membranes had poor proton conductivity, while SPEEK-7 membranes had acceptable conductivities, but poor mechanical stability due to excessive swelling. In the case of perfluorinated polymer electrolytes, the membrane remains mechanically strong even at high water uptakes due to its hydrophobic backbone. In polymer electrolytes based on hydrocarbon polymers, the water molecules of hydration are completely dispersed, while in perfluorinated membranes they have a spontaneous hydrophilic/hydrophobic separation [30]. This structural drawback makes SPEEK membranes with high sulfonation levels a poor choice as electrolytes for fuel cells. Membranes with high sulfonation levels also show lower thermal decomposition temperatures [1]. For these reasons, only SPEEK-5 membranes and its composites were chosen for conductivity and fuel cell studies. Furthermore, only composite membranes with 10% additive loading were tested for each additive.

Resistances were measured by the current interrupt technique, and conductivities were estimated from the cell constant. At least three MEAs of each type were tested for estimation of membrane resistance and hence through-plane proton conductivity. The standard error has also been shown in the figure. The reason for larger error bars in the proton conductivity of SPEEK composite membranes is the heterogeneity that results due to additive agglomeration during membrane casting.

Fig. 5 gives the conductivity data at 80°C for 75% and 50% inlet relative humidities (RHs). SPEEK/silica compos-

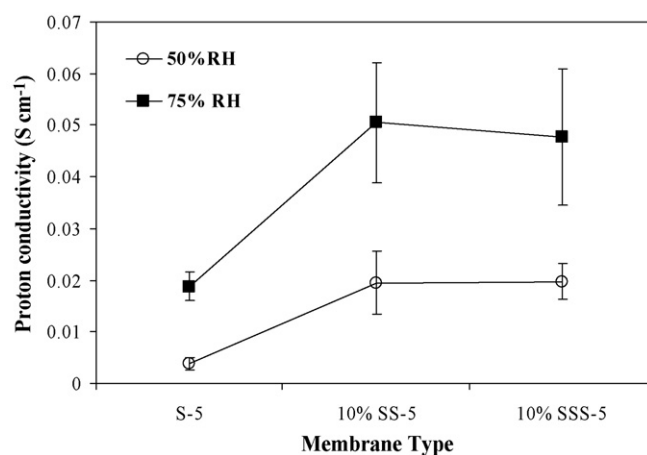


Fig. 5. Proton conductivity of S: SPEEK, SS: silica/SPEEK and SSS: sulfonic acid functionalized silica/SPEEK.

ite membrane (10% SS-5) shows a higher conductivity than SPEEK membranes (S-5). There is no appreciable difference in the conductivity of SPEEK/sulfonic acid functionalized silica membrane (10% SSS-5) to that of 10% SS-5 membranes. The conductivity of 10% SSS-5 was expected to be higher because of the added effect of proton conductivity enhancing SO_3 groups. The lack of increase is attributed to the large particle size and hence lower surface to volume ratio of the additive particles (as discussed in Section 3.4), which implies that most of the sulfonic acid groups in the additive are in the bulk as opposed to the surface. The surface/volume ratio is a key parameter for enhancing conductivity through silica functionalization and our current efforts are geared towards reducing additive particle size and enhancing surface to volume ratio in an attempt to further improve conductivity of SSS composite membranes.

The enhancement in conductivity upon addition of silica and sulfonated silica can be rationalized using prior reports in the literature [63–65]. This phenomenon has been observed by Kim et al. [64] in composite PEMs based on heteropolyacid in sulfonated polysulfones. The presence of the additive was found to enhance the proton conductivity, while at the same time decreasing the water uptake [63,64]. They have interpreted the lower water uptake as being due to incomplete removal of water from the membrane under the drying conditions applied. This is attributed to strong interactions between the sulfonic acid group in the polymer and the additive. The enhanced proton conductivity is attributed to the retention of water. Similarly, Karthikeyan et al. [65] reported increasing proton conductivity, but lower water permeation upon addition of silica to SPEEK (until a loading of 10 wt% is reached). They too attribute the higher proton conductivity of the composite membranes to the enhanced ability of the additive particles to retain water. The conductivity results obtained in this study are very similar to those reported in the above studies and it is likely that a similar mechanism is in place. This is consistent with water uptake measurements—the lower water uptake observed can also be attributed to the ability of silica and sulfonated silica to hold on to water molecules even at elevated temperatures.

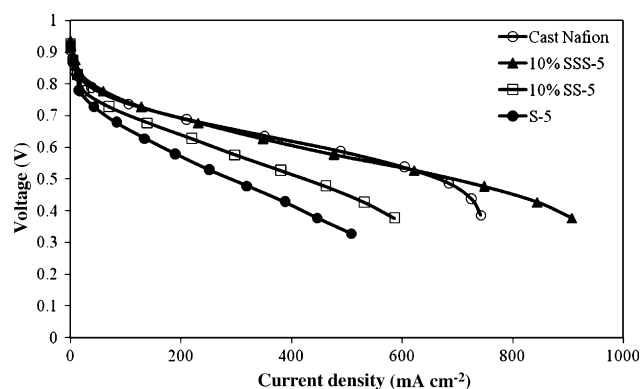


Fig. 6. Polarization curves at 80 °C and 75% RH. Anode: H₂, 0.2 slpm and Pt, 0.2 mg cm⁻²; cathode: air, 0.2 slpm and Pt, 0.4 mg cm⁻²; $P = 1$ atm.

3.7. Fuel cell performance curves

Polarization curves for MEAs made using four membranes (S-5, 10% SS-5 and 10% SSS-5, cast Nafion[®]) were recorded at 80 °C and 75% RH (Fig. 6) and 50% RH (Fig. 7) for H₂/air operation. The MEAs were prepared with approximately the same Pt loading (cathode: 0.4 mg cm⁻² and anode: 0.2 mg cm⁻²). In all cases the OCV was 900 ± 20 mV. It must be clearly noted that MEA performance does not directly correlate to membrane effectiveness—various contributing factors like membrane thickness, catalyst loading, electrode structure and mass transport limitations in the electrode will influence performance, in some cases even more than membrane resistance alone. For example, for the MEAs described in Figs. 6 and 7, the membrane *iR* compensated polarization curves at 50% RH also showed that the SSS-5 based MEA outperformed the SS-5 based MEA. This is evidently due to differences in the cathode layer and has nothing to do with the membrane itself. The appropriate measure of membrane efficacy should be Fig. 5. That said, the purpose of showing the performance data is to demonstrate that the SPEEK and SPEEK composite membranes can be used in an operating fuel cell environment and can be operated at lower relative humidities (75% and 50%) while achieving performances not far removed from what can be achieved with Nafion[®] membranes if MEAs (especially electrodes) are prepared with care.

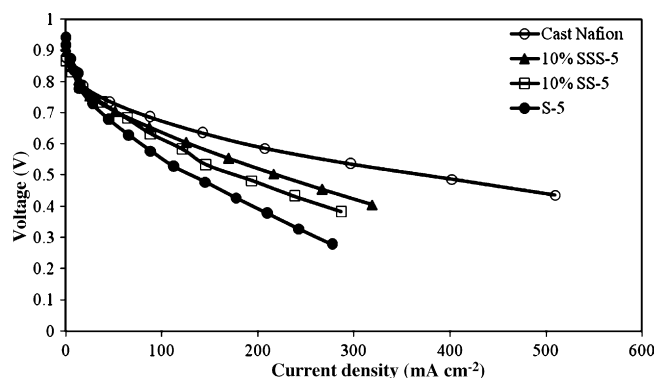


Fig. 7. Polarization curves at 80 °C and 50% RH. Anode: H₂, 0.2 slpm and Pt, 0.2 mg cm⁻²; cathode: air, 0.2 slpm and Pt, 0.4 mg cm⁻²; $P = 1$ atm.

The mechanical stability of SPEEK membranes was observed to be lower than Nafion[®] membranes, especially at high IECs. In the future, we propose to exploit the conductivity enhancing properties of the additive by incorporating them into SPEEK membranes with much lower IECs (which are more robust) to develop composite membranes that have conductivities similar to those reported in this paper, but are more mechanically robust.

4. Conclusions

Sulfonated PEEK of three different IECs was prepared at room temperature by reacting PEEK with sulfuric acid. Sol-gel derived silica additives: (1) silica and (2) silica functionalized with sulfonic acid (–SO₃H), were synthesized and SPEEK/silica and SPEEK/sulfonic acid functionalized silica composite membranes of three SPEEK IECs were cast with two additive loadings, 5% and 10%. The silica additives were characterized by FTIR and the presence of sulfonic acid groups on silica and the thiol to sulfonic acid transition were confirmed. A decrease in liquid water uptake was observed in the composite membranes (when compared to pure SPEEK of the same IEC). However, the proton conductivity of the composite membranes was found to be higher than pure SPEEK at a given IEC. This was similar to phenomena previously reported in the literature and was attributed to additive particles retaining water even under dry conditions. There was no appreciable difference between the conductivity of SPEEK/silica and SPEEK/sulfonic acid functionalized silica membranes. This was attributed to the large additive particle size due to agglomeration resulting in a very low surface to volume ratio and consigned most of the additional sulfonic acid groups to the bulk of the additive as opposed to the surface. Agglomeration was confirmed by SEM studies. At 80 °C and 75% RH the measured conductivity was 0.05 S cm⁻¹ for SPEEK-5 containing 10% sulfonic acid functionalized silica and 0.02 S cm⁻¹ for the plain SPEEK-5 membrane. At 80 °C and 50% RH the measured conductivity was 0.018 S cm⁻¹ for SPEEK-5 with 10% sulfonic acid functionalized silica and 0.004 S cm⁻¹ for the plain SPEEK-5 membrane. MEAs prepared with SPEEK composite membranes were tested in an operating fuel cell environment at 80 °C and 75% and 50% RH. The MEA results do not directly track with conductivity measurements because of differences in membrane thickness and differences in cathode activity between MEAs. Future directions will include enhancing additive surface to volume ratio through in situ additive generation, and testing composite SPEEK membranes for methanol permeability and in DMFCs.

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