Research Article

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Sulfonated poly(arylene ether sulfone) functionalized polysilsesquioxane hybrid membranes with enhanced proton conductivity

<https://doi.org/10.1515/epoly-2020-0048>
received June 30, 2020; accepted July 21, 2020

Abstract: Sulfopropylated polysilsesquioxane and –COOH containing fluorinated sulfonated poly(arylene ether sulfone) composite membranes (SPAES-SS-X) have been prepared via an *in situ* sol–gel reaction through the solution casting technique. The composite membranes showed excellent thermal and chemical stability, compared to the pristine SPAES membrane. The uniform dispersion of the sulfonated SiOPS nanoparticles on the polymer matrix was observed from the scanning electron microscope images. Atomic force microscopy and transmission electron microscopy images indicated significantly better phase-separated morphology and connectivity of the ionic domains of the composite membranes than the pristine SPAES membrane. The composite membranes showed considerable improvement in proton conductivity and oxidative stability than the pristine copolymer membrane under similar test conditions.

Keywords: sulfonated silica, composite membrane, thermal stability, membrane morphology, proton conductivity

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are used in residential and automobile sectors because of their eco-friendly nature and energy conversion efficiency. Proton exchange membrane (PEM) in PEMFCs acts as a separator between electrodes, facilitates proton transfer, and provides a barrier for fuel gas, oxidant, and electrons. Over the past few decades, a perfluorosulfonic

acid polymer such as Nafion[®] is the most cited PEM material due to its high proton conductivity and good chemical and mechanical stabilities (1,2). But high gas permeability, low operating temperature (<80°C), and high cost of the Nafion[®] membrane have led to rigorous research efforts in the development of an alternative aromatic semifluorinated sulfonated polymer, such as poly(arylene ether)s (3–5), poly(arylene ether sulfone)s (6–12), poly(aryl ether ether nitrile)s (13), poly(arylene sulfide sulfone)s (14,15), poly(arylene ether ketone)s (16–18), poly(aryl ether ether ketone)s (19,20), poly(aryl ether ether ketone ketone)s (21,22), polyimides (23,24), polytriazoles (25,26), and polybenzimidazoles (27,28).

To improve some of the inadequate properties of PEMs, an efficient and convenient approach has been considered by forming hybrid materials such as organic–inorganic nanocomposites. Usually, sulfonated polymers/copolymers filled with inorganic nanofillers show lower ion exchange capacity (IEC) values and subsequently reduce the proton conductivity of the PEMs (29–31). The hydrophilic fillers, such as SiO₂, TiO₂, and ZrO₂, are generally added to improve the water retention ability and enhance the proton conductivity of the PEMs (32–34). It envisioned that the introduction of these hygroscopic inorganic nanoparticles into the polymer matrix improves the hydration of the membrane and reduces the evaporation of water. Marani et al. synthesized titania nanosheets (TNS) and investigated the effects of TNS as an additive in sulfonated (poly ether ether ketone) (SPEEK) nanocomposites. They reported that the composite membrane with 1.67 wt% TNS showed a maximum conductivity value at 100% relative humidity (RH), which is much higher than that of a pure SPEEK membrane under the same conditions. In contrast, the degree of volume swelling was reduced by 80% to that of the reference SPEEK membrane (35).

In recent times, sulfonated nanofillers are being used as an additive to compensate for the reduction in IEC_w values with the addition of inorganic fillers to PEMs. Rhee et al. prepared sulfonated montmorillonite

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(SO₃H-MMT) and developed a composite electrolyte membrane with Nafion[®] 115. The proton conductivity of the composite membrane was slightly lower than that of pristine Nafion[®] 115 (36). Bebin et al. synthesized Nafion[®] 115/sulfonic acid groups containing Laponite nanocomposite membranes and reported higher proton conductivity and water retention ability than pristine Nafion[®] 115 (37). Sua et al. reported a similar result toward proton conductivity when sulfonated silica nanoparticle (s-SNP) was added to the poly(phthalazine none ether ketone) (SPPEK) membrane (38). A 3.6-fold increase in proton conductivity than pristine SPPEK membrane was reported when 7.5 phr of silica-SO₃H was added. Nevertheless, the conductivity value of the composite membrane was still lower than that of Nafion[®] 117. Later on, Xu et al. synthesized a series of new Nafion-based composite membranes via an *in situ* sol-gel reaction of 3-(trihydroxysilyl)propane-1-sulfonic acid (THSPSA) through the solution casting technique. More significantly, the composite membranes exhibit an increased water uptake and two times higher proton conductivity, compared to unmodified Nafion at high temperatures and low humidity (39). All these studies indicated that the composite approach might be an alternate way to enhance the PEM properties (40,41).

The main objective of the present research work was to exploit the effect of incorporated inorganic compounds in the presence of -COOH functionalized sulfonated polymers and fabricated highly proton-conducting hybrid membranes. Accordingly, a -COOH functionalized fluorinated sulfonated copolymer was prepared. Different amounts of THSPSA were added to this -COOH functionalized copolymer to make hybrid membranes by *in situ* sol-gel reactions of THSPSA during the film casting step (shown in Figure 1). The oxide precursor THSPSA was chosen due to its multi-functional structure. In contrast, the -COOH functionalized fluorinated sulfonated copolymers were selected for better interaction between the inorganic phases (-OH groups) and the ionic domains of the polymer matrix through -COOH groups. Besides, the sulfonic acid groups of the sulfonated poly(arylene ether sulfone) chains and the resulting sulfopropylated polysilsesquioxane (SiOPS) interacted with each other and formed a network structure, which was responsible for efficient proton-conducting channels. Thus, the utility of the newly prepared composite membranes (regarded as SPAES-SS-X, where X represents the theoretical amount in wt% of sulfonated silica in the hybrid membrane) has been demonstrated by investigating the morphology and selected PEM properties such as proton conductivity,

water uptake, mechanical strength, swelling ratio, and thermal and chemical stability.

2 Experimental section

2.1 Materials

The bishydroxy monomer, 2-[bis-(4-hydroxyphenyl)-methyl]-benzoic acid (TP-COOH), and the -CF₃ functionalized monomer, 4,4'-bis(4'-fluoro-3'-trifluoromethyl benzyl)biphenyl (QBF), were prepared, according to procedures reported in the literature (42,43). THSPSA (35 wt% in water) and 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS, >98%) were purchased from Fluorochem and Chemos GmbH, respectively, and were used as received. *N*-Methyl-2-pyrrolidone (NMP; E. Merck) was purified by stirring with NaOH and distilled (twice from phosphorus pentoxide [P₂O₅]) under vacuum before use. Toluene (Merck) was refluxed over filamentous sodium to remove water and was freshly distilled prior to use. Potassium carbonate was dried under vacuum at 120°C for 24 h before use. Other chemicals were used as received without any further purification.

2.2 Synthesis of the -COOH functionalized fluorinated sulfonated poly(arylene ether) copolymer

The -COOH functionalized fluorinated sulfonated poly(arylene ether) copolymer (TPQSH-COOH-50) was synthesized via standard K₂CO₃-mediated polycondensation of a bisphenol monomer (TP-COOH) with two bishalide monomers (QBF and SDCDPS) in the ratio of 50:50 where the NMP and toluene were used as solvent and cosolvent, respectively. The detailed synthetic procedure with characterization of TPQSH-COOH-50 has been demonstrated in an earlier publication (44). The copolymer structure used in this investigation is shown in Figure 2.

2.3 Composite membrane preparation

The composite membrane is prepared using the following procedure. A measured amount of TPQSH-COOH-50 copolymer was dissolved in 15 mL of DMAc and

Figure 1: Architectural representation of the preparation of SPAES-SS-X composite membranes through the formation of an IPN structure.

Figure 2: Chemical structure of the pristine copolymer TPQSH-COOH-50 (44).

filtered to obtain a transparent polymer solution. THSPSA (2.5–10 wt%) was added dropwise under vigorous stirring to this solution. The resulting mixture was sonicated for 30 min using a water bath sonicator. The homogeneous mixture was transferred into a round-bottomed flask for partial esterification reaction (between

the -COOH group of the polymer and the -OH group of the silica filler), which was carried out at 80°C for 12 h in DMAc with 5 mg of *p*-toluenesulfonic acid per gram of polymer for catalysis.

The resulting solution with different amounts of THSPSA was cast onto a glass petri dish and heated at

80°C for 12 h to complete the esterification process as well as to form a Si–O–Si network. Then the temperature was slowly increased to 100°C, 120°C, 140°C, and 160°C, and the membranes were kept for 2 h in each temperature to remove any residual solvent. After cooling down to room temperature, the composite membranes were peeled off from the glass plate and acidified by immersing in the 1.5 M H₂SO₄ solution at room temperature for 24 h, followed by washing with deionized (DI) water several times until pH 7. All the hybrid membranes were dried under vacuum overnight at 120°C before use. The typical thickness of the membranes was in the range of 45–50 µm.

3 Characterization

Infrared spectra of the composite membranes were recorded on a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer under a humidity-free atmosphere at room temperature. The DSC measurements were performed under nitrogen atmosphere using TA Instruments DSC Q20 at a heating rate of 20 K/min and the glass transition temperatures (T_g) determined by taking the middle point of the step transition in the second heating run. Low-temperature dynamic scanning calorimetry (DSC) measurements were performed to determine the state of water (the frozen water content and the nonfrozen water content) within the polymer membranes using a NETZSCH DSC 200PC instrument at a heating rate of 5 K/min under nitrogen atmosphere. Initially, 5–10 mg swollen membranes were sealed hermetically in a sample pan and cooled to –40°C. Then after reaching the equilibrium, the sample was heated to 40°C. The single melting enthalpy peak (enthalpy of fusion) that arose near 0°C was considered in order to determine the amount of free water present in the membrane during the course of the experiment (an average value was taken for calculation). Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ50 thermal analyzer under synthetic air (N₂:O₂ = 80:20) at a heating rate of 10 K/min. The mechanical properties of the acid form of the hybrid membranes (10 mm × 25 mm) were measured using a TINIUS OLSEN tensile testing machine (Model No. H5KS). The measurements were performed at a crosshead speed of 5 mm/min of the specimen length. All the membranes were predried at 80°C for 4 h before testing and the measurements were performed at 30°C and 60% RH. The IEC_w, water uptake, swelling ratio, and oxidative stability of the membranes were determined, according to the reported protocol (11,14). The surface images of the composite

membranes were taken using a field emission scanning electron microscope manufactured by Carl Zeiss, Model Supra 40. The instrument was operated at an accelerated voltage of 5–20 kV equipped with an energy-dispersive spectrometer. The atomic force microscopy (AFM) analysis was carried out using AFM 5500 (Agilent Technology) in tapping mode. Transmission electron microscopy (TEM) images of the ultra-microtome membranes were taken by using an FEI-TECNAI G2 20 S-TWIN TEM instrument at an operating voltage of 80 kV. The acid form of the membranes was stained with Pb²⁺ ions using 0.5 M lead acetate solution for overnight to enhance the contrast between phases. The membranes were then washed with DI water several times to remove the surface salt solution and dried at room temperature for 24 h. The stained samples were sectioned by ultra-microtome under cryogenic condition and placed on carbon-coated copper grids before TEM viewing. In plane, proton conductivity (σ , mS/cm) of all the composite membranes was measured at different temperatures by four-probe AC impedance spectroscopy using an electrode system connected to a Gamry instrument reference 3000 potentiostat/galvanostat/ZAR over the frequency range of 100 Hz–1 MHz under fully hydrated condition (11,12). The reproducibility in the measurements of proton conductivity was within 2–3%, and the maximum value obtained is reported.

4 Results and discussion

The formation of sulfopropylated polysilsesquioxane in all the composite membranes was confirmed by the FT-IR spectra, as shown in Figure 3. The characteristic symmetric stretching and asymmetric stretching bands at 809 and 1,018 cm^{–1}, respectively, suggest the formation of the Si–O–Si bond in the polymer composite (45). Additionally, the formation of polysilsesquioxane was also confirmed by the disappearance of Si–OH bands around 930–940 cm^{–1}. The aromatic C=C stretching band appeared at 1,584 cm^{–1}, whereas the C–F stretching band was found at 1,240–1,127 cm^{–1} (46). The characteristic symmetric stretching band at 1,051 cm^{–1} corresponds to the ether linkage of the polymers. The symmetric stretching of the aromatic S–O bond of the –SO₃H group overlaps with the asymmetric stretching of the Si–O–Si bond, but a strong absorption band was found at 1,095 cm^{–1} which corresponds to the asymmetric stretches of the aromatic S–O bond of the –SO₃H group. Moreover, the absorption band of S–O stretching from the –SO₃H group of sulfopropylated polysilsesquioxane

Figure 3: FT-IR spectra of SPAES-SS-X hybrid membranes.

at $1,125\text{ cm}^{-1}$ was superimposed with the C–F stretching band of the pristine copolymer. All these results suggest that the sulfopropylated polysilsesquioxane was successfully developed into the polymer matrix during the sol–gel process.

The hybrid membranes do not show any noticeable signature for glass transitions in the DSC analysis (temperature range of $100\text{--}350^\circ\text{C}$) attributed to the locking of the segmental motion caused by the ionic interactions of the hydrophilic sulfonic groups of both SiOPS and the sulfonated poly(arylene ether sulfone) chains (12,44,46). All hybrid membranes displayed two-step degradation profiles in TGA (Figure 4) under air. The first weight loss ($280\text{--}320^\circ\text{C}$) was assigned to the degradation of sulfonic acid groups. The 10% weight loss temperature of hybrid membranes was around 320°C and was lower than that of the pristine membrane (44). However, no significant change in 10% weight loss temperature of the hybrid membranes with the loading percentage of sulfonated SiOPS nanoparticles was observed. The weight loss range from 495 to 508°C was attributed to the decomposition of the polymer backbone (Table 1).

Mechanical stability is critical of the electrolyte membranes for effective utilization in a fuel cell as PEMs. Table 1 summarizes the mechanical properties of the composite membranes and the pristine membrane and Nafion® 117. Figure 5 shows that all the composite membranes exhibit a lower tensile strength value than the --COOH functionalized pristine copolymer membrane. The existence of additional $\text{--SO}_3\text{H}$ groups in the polymer matrix and the higher structural rigidity of the

Figure 4: TGA curves of the SPAES-SS-X composite membranes in air.

inorganic nanofillers make them mechanically weak (33). In general, all these hybrid membranes showed higher tensile strength and Young's modulus with a lower elongation at break than Nafion® 117. In the dry state, the tensile strength values of SPAES-SS-X hybrid membranes decreased steadily with the increase in filler loading, but no absolute trend was observed in Young's modulus and elongation at break values. The membranes with 7.5 wt% (SPAES-SS-7.5) filler loading showed an optimal set of mechanical properties with elongation at break as high and sufficient for fabricating a membrane electrode assembly (47,48).

Oxidative stability of the hybrid membranes was checked by immersing the samples in Fenton's reagent (3 wt% H_2O_2 , 2 ppm FeSO_4) at 80°C (Table 1). The hybrid membrane with 2.5 wt% filler exhibited the highest oxidative stability, with $\tau_1 = 22.5\text{ h}$, whereas the least oxidative stability was observed for 10% filler loaded membrane ($\tau_1 = 7.5\text{ h}$). Generally, compared to the pristine membrane, the oxidative stability of the hybrid membranes increases with increasing filler loading. Here, the presence of additional $\text{--SO}_3\text{H}$ groups in the nanofiller reduces the oxidative stability of the membranes. Hydrophilic domains are prone to an oxidative attack by the free radical species ($\text{HO}^\bullet$ and $\text{HOO}^\bullet$). Thus, increasing the percentage of s-SNPs (THSPSA) increases the number of hydrophilic domains, and consequently, the oxidative stability of the hybrid membranes with higher filler loading decreases. However, due to the formation of the crosslinked and interpenetrating network structure, the hybrid membrane, even with 10 wt% filler, showed excellent oxidative stability, compared to many other pristine membrane materials (24,44,46). On the other hand, the --CF_3 groups in QBF and the wholly

Table 1: Thermal, mechanical, and oxidative stability of SPAES-SS-X membranes as well as selected reference polymers

Polymer	T_g^a (°C)	T_d^b	TS ^c (MPa)	YM ^d (GPa)	EB ^e (%)	Oxidative stability τ^f (h)		Ref.
						τ_1	τ_2	
TPQSH-COOH-50	—	510 ^g	52 ^g	1.68 ^g	8 ^g	21.2 ^g	>24 ^g	(44)
SPAES-SS-2.5	—	508	47	1.54	6	22.5	>24	This study
SPAES-SS-5.0	—	505	39	1.41	3	18.0	>24	This study
SPAES-SS-7.5	—	501	36	1.39	10	15.5	>24	This study
SPAES-SS-10	—	495	27	1.64	2	7.5	>24	This study
Nafion® 117	129	435	21.9 ^h	0.16 ^h	288 ^h	>24 ^h	—	(12)

^a Glass transition temperature determined by the DSC. ^b Backbone degradation temperature. ^c Tensile strength at a strain rate: 5%/min, 65 ± 2% RH, and 30°C. ^d Young's modulus. ^e Elongation at break. ^f τ_1 and τ_2 refer to the initial breaking time and the time to complete dissolution in Fenton's reagent (2 ppm FeSO₄ in 3% H₂O₂) at 80°C, respectively. ^g Data from (44). ^h Data from (12).

Figure 5: Stress-strain plot of the hybrid membranes.

aromatic nature of the copolymers are mainly responsible for enhancing the oxidative stability and making them resistant toward attack by the oxidative species (49).

The hydrolytic stability of the hybrid membranes was investigated at 80°C, keeping them for 24 h in water. The membranes were substantially stable in wet conditions, as no apparent changes were observed in their appearance and weight even after 24 h. Although the SiOPS alone dissolves immediately in hot water, the hybrid membranes exhibit a high hydrolytic stability. This stability arises from a strong interaction (possibly hydrogen bonding) between the sulfonic acid groups of SiOPS and the sulfonated poly(arylene ether sulfone) chains (50).

IEC_w usually signifies the number of exchangeable protons present in the polymer electrolytes and was measured by the classical titrimetric analysis with 0.1 M NaOH solution. The IEC_w values of SPAES-SS-X copolymer

membranes and Nafion® 117 are given in Table 2. The titrimetric IEC_w value of the bare TPQSH-COOH-50 was found to be 1.32 mequiv./g, and with an increase of THSPSA loading, the IEC_w was found to increase rapidly up to 1.48 mequiv./g, but a further rise in THSPSA content from 7.5 to 10 wt% did not lead to a noticeable increase in IEC_w. It is attributed to the trapping of H⁺ ions (present in the inner sulfonic acid groups) by large SiOPS nanoclusters at high precursor concentrations (39). This result corroborates with the water uptake of the hybrid membranes. The water uptake values of the hybrid membranes were significantly higher than that of the pristine TPQSH-COOH-50 membrane, which is attributed to the hygroscopic nature of the SiOPS nanofiller (39). With increase in THSPSA loading up to 7.5 wt%, the water uptake values gradually increased from 47% to 61% (at 80°C). Beyond 7.5% loading of THSPSA, the rise in water uptake of the SPAES-SS-10 hybrid membrane increased marginally (64%), as shown in Figure 6a.

A low-temperature DSC experiment was performed to investigate the state of water inside the hydrated membranes by measuring the latent heat of fusion (ΔH_f) for water (44). Generally, a higher ΔH_f value indicated a high concentration of free and weakly bound waters that are responsible for the melting enthalpy peaks near 0°C in the DSC curves. It is consistent with the literature reports claiming that the loosely bounded interfacial water molecules are mainly responsible for the interconnected channels between ionic domains and play a crucial role in proton conduction of Nafion® (2,51). In contrast with Nafion® 117 (39), the SPAES-SS-2.5 membrane showed a sharp melting peak near 0°C, which is attributed to a more significant number of free and weakly bound water molecules in it (Figure 6b). However, the same behavior was not observed with the hybrid membranes when the filler loading increased to 5 wt% or higher. It could be observed that due to the

Table 2: IEC_w, hydration number, water uptake, and proton conductivity of pristine copolymer, SPAES-SS-X composite membranes, and Nafion® 117

Polymer	IEC _w (meq/g)		λ^b [H ₂ O/SO ₃]		WU ^c (wt%)		Swelling ratio (%) In plane	σ^d (mS/cm)		E_a (kJ/mol)
	Theo. ^a	Tit.	30°C	80°C	30°C	80°C		30°C	80°C	
TPQSH-COOH-50	1.38	1.32	—	—	24	32	16	30	55	9.6
SPAES-SS-2.5	1.38	1.36	17	19	43	47	3	38	93	15.6
SPAES-SS-5.0	1.38	1.41	19	21	47	52	5	40	114	18.8
SPAES-SS-7.5	1.38	1.48	23	25	57	61	9	53	130	16.0
SPAES-SS-10	1.38	1.50	24	26	59	64	10	54	138	16.7
Nafion® 117	0.91	0.90	—	—	—	—	—	93	165	10.2

^a IEC_{w,Theo.} = (1,000/MW_{repeat unit}) × DS_{Theo} × 2, where DS_{Theo} is calculated theoretically from a monomer feed ratio. ^b λ = WU_w (%) / (100 × IEC_{w,Theo.} × M_{w,H₂O}), where M_{w,H₂O} = 18 g/mol. ^c WU(wt%) = [(W_{wet} - W_{dry})/W_{dry}] × 100. ^d Proton conductivity was measured under fully hydrated condition (in water).

presence of highly dense sulfonic acid groups, the hybrid membranes with more filler loading contain a higher number of strongly bonded water molecules (probably through hydrogen bonding) and do not contribute to the melting endotherm in the DSC curves. The hydration number (λ , the average number of water molecules per sulfonic acid group) of the hybrid membranes was calculated to probe the state of water inside the hydrated membranes. From Table 2, it is seen that at 80°C, with an increase in THSPSA, the hydration number (λ) sharply increased from 19 to 25 for SPAES-SS-7.5 and then slowly to 26 for SPAES-SS-10.

Analogous to the water uptake, the swelling ratios (in-plane) of the SPAES-SS-X hybrid membranes gradually enhanced with increasing sulfonated silica nano-filler loading and temperatures. However, compared to

the pristine copolymer membrane, the hybrid membranes showed a much lower-dimensional swelling attributed to the formation of a cage-like structure of the silica network. They suppressed the free movement of water molecules through the bulk of the polymer (52). At 80°C, all the hybrid membranes possess a much better dimensional stability than Nafion® 117, resulting from the bulky TP-COOH groups and hydrophobic -CF₃ groups along with a rigid quadriphenyl moiety (18).

Scanning electron microscope (SEM) techniques have extensively studied the surface morphology of the hybrid membranes to examine the homogeneity of the silica sulfonic acid nanoparticles (THSPSA) in the polymer matrix. The SEM image (Figure 7) reveals that the s-SNPs were uniformly dispersed on the polymer surface, indicating homogeneity. The compatibility between the

Figure 6: (a) Variation in the water uptake (wt%) with % of THSPSA at different temperatures of SPAES-SS-X composite membranes. (b) DSC melting curves of water-swollen membranes of TPQSH-COOH-50 and SPAES-SS-2.5.

organic and inorganic components improved, probably due to the existence of two types of covalent bonds (the sulfonated silica particles formed the covalent bonds with a $-\text{COOH}$ functionalized polymer and the bond was formed after the formation of SiOPS) present in the hybrid membranes. The density of the $-\text{SO}_3\text{H}$ groups on the membrane surface gradually increases with a gradual increase in silica loading (2.5–10 wt%). In addition to that, the surface morphology of the composite membranes was studied by AFM in tapping mode (Figure 8). There are two regions in the AFM image where the bright part corresponds to the hard hydrophobic domains and the dark area corresponds to the soft hydrophilic domains. The interconnectivity of the ionic domains was vividly observed in the composite membrane, with 7.5 wt% of silica loading.

The bulk morphology of the membranes played an important role in elucidating the proton conductivity and in being investigated by the TEM. The Pb^{2+} -stained sample membranes showed (Figure 9) an excellent micro-phase separated morphology wherein the dark spherical regions correspond to the hydrophilic ionic

domains. The brighter areas represent the hydrophobic nonionic domains of the polymer matrix. However, the connectivity of the ionic domains of the composite membranes was significantly better than that of the pristine SPAES membrane (44). The hybrid membranes with 2.5 wt% SiOPS consist of both small hydrophilic clusters (particle size $\sim 20\text{--}25\text{ nm}$) and some interconnected medium-sized ionic clusters (particle size $\sim 40\text{--}45\text{ nm}$). The connectivity of the ionic domains was more pronounced on increasing the percentage of hydrophilic silica nanoparticles. It is believed that the ionic domains resulted from the aggregation of sulfonic acid groups from the polymer electrolyte and THSPSA/SiOPS, and the maximum interconnectivity was found in the SPAES-SS-10 composite membrane. The result suggests that the SiOPS aggregates distributed relatively more uniformly to form a well-dispersed nanocomposite membrane.

Proton conductivity is the prime property for a PEM material for its effective utilization in fuel cells. In plane, proton conductivity of all the composite membranes was measured using AC impedance spectroscopy within the temperature ranging from 30 to 80°C under fully

Figure 7: SEM images of SPAES-SS-X composite membranes.

Figure 8: 2D tapping mode AFM images SPAES-SS-*X* composite membranes.

hydrated condition. In comparison with the pristine TPQSH-COOH-50, the hybrid membranes exhibited an improved proton conductivity due to the presence of additional sulfonic acid groups in nanoparticles. Table 2 summarizes the proton conductivity of the membranes, and Figure 10a represents the change in proton conductivity of the composite membranes as a function of temperatures along with Nafion® 117.

The proton conductivity increases progressively with the loading of the THSPSA content, as shown in Figure 10b and, in particular, the conductivity of the hybrid membranes (mainly $XX = 7.5$ and 10) at low temperature was significantly improved, compared to the pristine membrane (TPQSH-COOH-50). Depending on the amount of filler loading, the proton conductivity of the hybrid membranes was exhibited in the ranges of 38–54 mS/cm and 93–138 mS/cm, respectively, at 30°C and 80°C (Table 2). The 10 wt% SiOPS loaded membrane showed more than two times higher proton conductivity (138 mS/cm) than the pristine TPQSH-COOH-50 membrane (55 mS/cm) at 80°C under the same test conditions (44).

It is noted that the proton conductivity of this 10 wt% filler loaded membrane did not increase that sharply, compared to that of the 7.5 wt% SiOPS charged membrane. This feature was attributed to the trapping of inner $-\text{SO}_3\text{H}$ groups by forming a high precursor concentration of the large SiOPS nanoclusters in 10 wt% filler loaded membrane and making them inert for the interaction with water (50). The proton conductivity values are in close agreement with the water uptake values of the hybrid membranes. The proton transportation of hybrid membranes occurred by both surface and bulk transport paths. The protons hopped on the surface of the pore channels in the form of H_3O^+ in the surface transport pathway, whereas, in bulk transport mechanisms, the protons jumped in the bulk of the pore channels in the form of $\text{H}_5\text{O}_2^+/\text{H}_9\text{O}_4^+$ (53–55). The density of the functional groups and the distance between two neighboring functional groups control the rate of surface transport pathway, whereas the rate of bulk transport pathway was controlled by the RH of the membrane surroundings and the cross-sectional area of the pore channels. The incorporation of functionalized silica

Figure 9: TEM micrographs of lead (Pb^{2+}) stained SPAES-SS-X composite membranes.

(THSPSA) into the polymer matrix reduced the distance between two neighboring proton-conducting moieties, compared to the pristine TPQSH-COOH-50 membrane. It facilitated the surface transportation effectively through the

Figure 10: (a) Proton conductivity of bare copolymer and composite membranes. (b) Variation in proton conductivity with % of THSPSA at different temperatures under fully hydrated conditions of SPAES-SS-X hybrid membranes.

Figure 11: Temperature-dependent proton conductivity (σ) of the hybrid membranes.

hybrid membranes. For a better understanding, the temperature-dependent proton conductivity of the membranes is plotted in Figure 11.

The activation energies of composite membranes were calculated from the slope of different lines presented in Figure 11 using the Arrhenius equation and the values were found to be in the range of 15.6–18.8 kJ/mol, close to that of Nafion[®] 117. The activation energies of the composite membranes are higher than that of the pristine TPQSH-COOH-50. The hydrogen bond present in the crosslinked composite membranes needs to be broken at the high temperature to facilitate proton transport, resulting in relatively high activation energies (12). These results were in concurrence with the morphological data. They suggested that the incorporation of SiOPS evokes a significant improvement in the polymer electrolyte membranes' water transport behavior by forming an interconnected ionic network that causes high proton conductivity.

5 Conclusions

A series of fluorinated sulfonated hybrid membranes were fabricated using a practical approach to improve the proton conductivity by a simple incorporation of an acid-functionalized THSPSA nanofiller. The prepared hybrid membranes showed excellent mechanical stability. The SEM studies suggest that the sulfonated SiOPS nanoparticles were dispersed uniformly on the polymer matrix in all the hybrid membranes with high

homogeneity, probably due to the existence of two types of covalent bonds. However, the TEM micrographs of the composite membranes showed a clear phase-separated morphology with a significantly better connectivity of the ionic domains than the pristine SPAES membrane. The pendant sulfonic acids on the polysilsesquioxane fillers help to increase the interconnectivity of the proton transport channels by reducing the distance between two neighboring proton-conducting moieties, compared to the pristine TPQSH-COOH-50 membrane and facilitated the proton transportation effectively through the composite membranes. The SPAES-SS-10 membrane showed a maximum proton conductivity of 138 mS/cm at 80°C. This work demonstrates that the prepared nanocomposite conductive membrane materials are expected to find their applications in PEM fuel cells.

Acknowledgment: RM thanks the CSIR, New Delhi, for providing the fellowship to carry out this research.

Conflict of interest: One of the authors (Susanta Banerjee) is a member of the Editorial Advisory Board of *e-Polymers*.

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