ORIGINAL ARTICLE

Synthesis and characterization of sulfonated poly (arylene ether sulfone)/silicotungstic acid composite membranes for fuel cells

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A series of composite membranes based on sulfonated poly (arylene ether sulfone) (SPAES) embedded with powdered silicotungstic acid (STA) was synthesized. SPAES was synthesized by direct aromatic nucleophilic polymerization and then solution blended with STA. Fourier-transform infrared spectroscopy analysis showed that the sulfonic acid groups on the polymer backbone interacted with the tungstic oxide in STA. The composite membranes exhibited a low Heteropolyacid extraction after treatment with water at 60 °C for 24 h. The composite membranes were characterized for water uptake, ion-exchange capacity (IEC), hydrolytic stability, proton conductivity and thermal stability in order to evaluate the suitability of these membranes for fuel cells. The proton conductivity of the membranes increased with increasing STA content. With an increase in the STA content, the conductivity of the composite membranes at 30 °C increased from 0.079 to 0.109 S cm⁻¹, whereas the parent membrane exhibits a proton conductivity of 0.073 S cm⁻¹. The composite membranes not only had good proton conductivity but also showed excellent thermal stability and mechanical strength. This study shows that the composite membranes based on SPAES and STA can be viable candidates for electrolyte membranes.

Polymer Journal (2013) 45, 166–172; doi:10.1038/pj.2012.102; published online 13 June 2012

Keywords: composite membrane; fuel cell; proton conductivity; silicotungstic acid; sulfonated poly (arylene ether sulfone)

INTRODUCTION

Fuel cells are widely used as environmentally friendly and reliable power-generation devices for vehicles, transportation and portable devices.¹ The proton-exchange membrane (PEM) is a key component of the PEM fuel cell, which is an attractive energy-conversion device for portable power applications. A fuel cell membrane must have thermal, chemical and mechanical stability in addition to good proton conductivity. The stability of the membranes is related to the polymer backbone, and the proton conductivity of the membrane is related to its acid moiety. Polymers with differing chemical structures and various strategies for incorporating sulfonic acid groups have been explored for developing potential PEM materials.² Sulfonated poly (arylene ether sulfone)s (SPAESs) are good PEM materials because of their excellent mechanical strengths, good acid and thermal oxidative stabilities, and high proton conductivities. Perfluoro sulfonated polymer is widely used as the PEM in polymer electrolyte fuel cells because of its good chemical stability and high proton conductivity. Perfluoro sulfonated polymer electrolyte membranes have disadvantages in terms of synthetic difficulty, toxic

intermediates, loss of stability, conductivity at temperatures above 100 °C and high fuel cross-over.³ To overcome these problems, studies have been conducted on non-fluorinated hydrocarbon-based polymer electrolyte membranes such as poly (ether ether ketone),⁴ SPAES,^{5,6} sulfoalkylated polysulfones,⁷ sulfonated polyimide,⁸ sulfonated polystyrene,⁹ sulfonated poly (arylene ether ketone),¹⁰ and so on. These polymers have a lower production cost and good chemical and electrochemical stabilities.

Although improvements have been achieved using these types of polymers, the proton conductivity at elevated temperatures is still unsatisfactory because of the lack of water retention at temperatures much higher than 100 °C. The incorporation of various inorganic materials has been attempted to overcome the above-mentioned drawback. The incorporation of inorganic nanoparticles into a polymer matrix might improve proton conductivity,^{11,12} mechanical strength,^{13,14} fuel barrier properties¹⁵ and membrane durability.¹⁶ Composite organic–inorganic membranes are the most attractive polymer electrolyte membranes for fuel cells.^{11,13} Heteropolyacids (HPA) are one of the most attractive inorganic modifiers because of

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Received 22 September 2011; revised 13 March 2012; accepted 9 April 2012; published online 13 June 2012

their crystalline structure, which has been demonstrated to be highly conductive^{17,18} and thermally stable.^{19,20} In this manuscript, we report on the syntheses and characterization of SPAES/STA composite membranes for fuel cell applications. The influence of the dispersed silicotungstic acid (STA) on the membrane properties, such as water uptake, ion-exchange capacity (IEC), thermal and hydrolytic stability, HPA extraction after treatment with water and proton conductivity, was studied.

EXPERIMENTAL PROCEDURE

Materials

4,4'-Dichlorodiphenylsulfone (DCDPS), STA, *N,N*-dimethylformamide and *N,N*-dimethylacetamide were purchased from the Sigma-Aldrich Co. (St Louis, MO, USA). 4,4'-Bisphenol-A, potassium carbonate, *N*-methyl-2-pyrrolidone, methanol, toluene and isopropylalcohol were purchased from Sisco Research Laboratory Private Ltd. (Mumbai, India). Fuming sulfuric acid (20% SO₃) was purchased from S.D. Fine Chem. (Mumbai, India). The 3,3'-disulfonated 4,4'-dichloro diphenyl sulfone (SDCDPS) was synthesized from DCDPS and dried at 160 °C under vacuum for 16 h before use. DCDPS and bisphenol-A were dried at 100 °C under vacuum for 16 h before use. STA was dried at 100 °C in an air circulating oven for 12 h before use. All other chemicals were used as received.

Monomer synthesis

The synthesis of SDCDPS was performed according to a reported procedure.^{21,22} The aromatic disulfonation reaction was conducted in a three-necked round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet and outlet. Initially, the reaction set-up was purged with nitrogen for 30 min. Following this step, the purging was stopped during the reaction to minimize SO₃ losses. An amount of 0.1 mol of DCDPS (28.7 g) and 100 ml of fuming sulfuric acid (20% SO₃) were placed in a round-bottom flask. The reaction temperature was slowly raised from room temperature to 120 °C and maintained with constant stirring for 5 h. Then, the reaction mass was cooled to room temperature and slowly poured into an ice-water mixture (150 g ice + 150 g water). Eighty grams of NaCl was added to precipitate the

white crude material, which was redissolved into 300 g of de-ionized water. The solution was neutralized with 2.0 *N* NaOH until a neutral pH was reached. A total of 80 g of NaCl was added to the solution, then heated to 65 °C. The reaction was then slowly cooled to room temperature without stirring and placed into an ice-bath. The crude SDCDPS was filtered off and recrystallized from an isopropylalcohol/water mixture (9:1). The white SDCDPS material was dried at 160 °C under vacuum for 16 h.

Synthesis of sulfonated poly(arylene ether sulfone)

A typical polymerization procedure for the synthesis of sulfonated poly(arylene ether sulfone) was as follows: 12.0 mmol of SDCDPS (5.89 g), 8.0 mmol of DCDPS (2.29 g) and 20.0 mmol of BP-A (4.56 g) were added to a 250 ml three-necked round-bottom flask equipped with a magnetic stirrer, Dean-Stark trap and nitrogen inlet. A volume of 70.0 ml of *N*-methyl-2-pyrrolidone was added and well stirred until the monomers were dissolved. A volume of 35.0 ml of toluene and 25.0 mmol of anhydrous potassium carbonate (3.45 g) were added and refluxed at 150 °C for 5 h. Following this step, the temperature was slowly raised to 190 °C by the controlled removal of toluene from the reaction mixture. The polymerization was continued at 190 °C for 19 h. The viscous solution was cooled to room temperature and diluted with *N,N*-dimethylformamide to allow easier filtering. Then, the solution was filtered using 100-μm pore size filter paper to remove the majority of the potassium salts. The polymer solution was slowly added to a beaker containing an excess of methanol. The precipitated sulfonated polymer was washed several times with ethanol and then dried under vacuum at 100 °C for 24 h. The synthetic scheme of SPAES is shown in Figure 1.

Synthesis of SPAES/HPA composite membranes

The acidic form of the SPAES polymer (5 wt%) was first dissolved into *N,N*-dimethylacetamide at room temperature. After the complete dissolution of SPAES, a calculated amount of STA (10–40%) was added, stirred well and heated to 60 °C for 6 h. The composition used to synthesize the composite membranes is given in Table 1. The viscous solution was then cast onto a flat glass plate. The cast membranes were dried at 60 °C for 12 h, 90 °C for 18 h and 140 °C for 3 h. The resulting membranes were soaked in de-ionized water

Figure 1 Synthetic scheme of sulfonated poly (arylene ether sulfone).

Table 1 Composition and properties of SPAES/STA composite membranes

Polymer code	Composition (weight %)		IEC (meq g ⁻¹)	Water uptake (%)	Intrinsic viscosity at 25 °C (dl g ⁻¹)	Swelling ratio (%)
	SPAES	HPA				
SPAES/STA-0	100	0	2.13	46.5	1.62	7.21
SPAES/STA-10	90	10	2.07	42.3	1.57	6.84
SPAES/STA-20	80	20	1.93	37.5	1.53	6.13
SPAES/STA-30	70	30	1.85	34.9	1.47	5.64
SPAES/STA-40	60	40	1.80	31.2	1.44	5.05

Abbreviations: HPA, heteropolyacid; SPAES, sulfonated poly (arylene ether sulfone).

overnight to release the membranes from the glass plates. The membranes were thoroughly washed with de-ionized water and then dried at 100 °C for 16 h under vacuum.

Measurements

For the fourier-transform infrared spectra (FT-IR) analysis, the composite membranes were first dried at 100 °C under vacuum for 6 h to remove any moisture/solvents. Small pieces of the membranes were then cut for each measurement. The spectrum for each film was collected using a Nicolet Impact 400 FT-IR spectrophotometer. High performance liquid chromatography (HPLC) analysis was performed using a LC-10AT-VP, Shimadzu, Kyoto, Japan. Thermogravimetric analyses of the composite membranes were performed using a Thermo gravimetric analyzer (Q 50, TA Instruments, New Castle, DE, USA) at a heating rate of 20 °C per min in a nitrogen atmosphere. Intrinsic viscosity measurements were performed in *N*-methyl-2-pyrrolidone at 25 °C using a Capillary Viscometer, Schott Geräte, Postfach, West Germany. The IEC of the membranes was measured using the titration method. The composite membranes were soaked in 1.0 M HCl for 10 h to regenerate the protons from the salt form, if any. The membranes were thoroughly washed with de-ionized water several times and were then soaked in a 0.1 M NaCl solution for 16 h. The protons that were released from the exchange reaction with Na⁺ ions were titrated against a 0.01 M NaOH solution using a phenolphthalein indicator. The IEC was determined from equation (1).

$$\text{IEC (meq g}^{-1}\text{)} = \frac{X \times N_{\text{NaOH}}}{\text{Weight of the polymer}} \quad (1)$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

For the water uptake and swelling ratio studies, the acidified membranes were dried at 120 °C until constant weights and lengths were obtained, which are recorded as W_d and L_d . Then, the dried membranes were immersed into de-ionized water. The water attached to the surface was quickly swabbed with tissue paper before measurement. The length and weight were measured several times until constant measurements were achieved, which are denoted as W_w and L_w . The water uptake of the membrane was calculated using the equation (2).

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

The swelling ratio was defined as equation (3).

$$\text{Swelling ratio} = \frac{L_w - L_d}{L_d} \times 100 \quad (3)$$

The extraction of HPA was determined using a ultraviolet–visible spectrophotometer (HITACHI, Tokyo, Japan, U-2900). The freshly prepared, dry composite membranes were weighed and immersed into 25 ml of de-ionized water at 60 °C for 24 h. Following this step, the extracted solution was placed into a quartz cell and measured at 262 nm, which provides the maximum absorption spectrum. We can obtain the concentration of the extracted HPA (C) from the concentration-absorption ultraviolet–visible spectrum graph, and

the HPA extraction (%) was determined by using equation (4).

$$\text{HPA extraction (\%)} = \frac{C \times 25 \text{ ml}}{\text{Weight of HPA in sample}} \times 100 \quad (4)$$

The proton conductivity measurements of the membranes were performed in a two-probe cell using the AC impedance technique. The conductivity cell was comprised of two stainless steel electrodes; each electrode had a 20-mm diameter. The sample was sandwiched between the two stainless steel electrodes fixed in a Teflon block, and kept in a closed glass container. The AC impedance spectra of the membranes were recorded in the frequency range of 1–10 Hz with a perturbation voltage amplitude of 10 mV using an Autolab PGSTAT 30 (KM Zuidwest, The Netherlands). The resistance value associated with the membrane conductivity was determined from the high-frequency intercept of the impedance with the real axis. The measurements were conducted in the temperature range of 30–130 °C. The conductivity of the membranes was calculated by using the equation (5).

$$\sigma (\text{S cm}^{-1}) = \frac{L}{RA} \quad (5)$$

where σ is the proton conductivity of the membrane, L is the membrane thickness in cm, R is the membrane resistance and A is the cross-sectional area of the membrane. The tensile strength and Young's moduli of the fully hydrated membranes were measured using a Universal Tester, Instron, Norwood, MA, USA. Samples with a width of 20 mm and a length of 50 mm were tested using a 250 N load cell that was pulled at 50 mm min⁻¹ within a 21-cm gauge length. Triplicate analyses were performed and the average values were taken for determining the tensile strength and the Young's modulus.

RESULTS AND DISCUSSION

Spectral analysis

HPLC analysis confirms the absence of a starting material in SDCDPS. Figure 2 shows the chromatograms of DCDPS and SDCDPS. The reverse-phase HPLC analysis was performed by using the mobile phase in the proportion of methanol and water (80:20). The flow rate was set to 0.75 ml min⁻¹. The chromatograms were obtained at a wavelength of 254 nm by injecting 20 µl of 0.08 mg ml⁻¹ of both the standard and sample in a methanol medium. The retention time of DCDPS is 9.28 min, whereas that of SDCDPS is 2.91 min. Proton nuclear magnetic resonance (NMR) analysis was performed for the monomer (SDCDPS) and the polymer (SPAES) using dimethyl sulfoxide-*d*₆ as a solvent. The NMR spectra of the sulfonated monomer and the polymer are shown in Figures 3 and 4, respectively. FT-IR spectra of the SPAES and SPAES/STA-30 composite membranes are shown in Figure 5. The peaks at 1582 and 1476 cm⁻¹ are attributed to the vibrations of the aromatic ring skeleton. The aromatic C–C band at 1496 cm⁻¹ for SPAES was observed to split because of new substitution upon sulfonation. The new band at 1026 cm⁻¹ that appeared upon sulfonation was assigned to the sulfonic acid group in SPAES. The typical vibrations of the

Figure 2 The HPLC chromatograms of DCDPS and SDCDPS.

Figure 3 ^1H NMR spectrum of SDCDPS.

Figure 4 ^1H NMR spectrum of SPAES. DMSO, dimethyl sulfoxide.

Figure 5 FT-IR spectra of (a) SPAES and (b) SPAES/STA-30 composite membrane.

HPA molecules were observed around the W–O stretching region at 895 and 980 cm^{-1} , which are the absorption bands of W–O–W and W=O, respectively. These absorptions confirm the successful incorporation of STA into the polymer matrix.

Ion-exchange capacity

Generally, the proton conductivity and the water uptake of the membrane directly depend on the amount of the sulfonic acid group, and hence, the IEC of the polymer. However, the sulfonic acid groups not only result in the polymer being proton conducting but also make it hydrophilic. Hence, the polymer with higher sulfonic acid groups swells in humid conditions and loses its mechanical strength, which leads to membrane rupture. Therefore, controlling the amount of the sulfonic acid group is a prime concern. The IEC change with increasing STA content is presented in Table 1. It can be seen that the order decreased as SPAES/STA-0 > SPAES/STA-10 > SPAES/STA-20 > SPAES/STA-30 > SPAES/STA-40. As indicated from Table 1, with an increase in STA content, the weight of the SPAES is decreased, and hence there will be a lower amount of the sulfonic acid group in a particular weight of the polymer. This observation is the reason for decreasing IEC values with increasing STA content.

Water uptake

The water uptake of sulfonated polymers is known to have a profound effect on the proton conductivity and mechanical properties. An increase in water uptake generates a more solvated species, which is needed for the improvement of conductivity; however, a high water content produces mechanically less stable membranes. Here, the

water uptake follows the same trend as the IEC, and the values are provided in Table 1. It can be seen that the water uptake values decreased as SPAES/STA-0 > SPAES/STA-10 > SPAES/STA-20 > SPAES/STA-30 > SPAES/STA-40. The water uptake decreased with an increase in the STA content, although STA is a solid acid. The sulfonic acid groups form hydrogen bonding interactions with the water molecules, which leads to water uptake. The STA interacts with the sulfonic acid group and decreases the amount of free sulfonic acid groups available to form hydrogen bonds with water molecules. Hence, the water uptake directly depends on the amount of sulfonic acid groups. In the composite membranes, with an increase in the STA content, the SPAES amount decreases, and hence, the water uptake of the polymer decreases. The swelling ratio between the composite and parent membrane was analyzed and the values are presented in Table 1.

Thermal stability

The thermal stability of the composite membranes was measured using the thermogravimetric analyzer, and the thermograms are shown in Figure 6. All membranes showed a three-step degradation pattern. The first weight loss was observed at approximately 100 °C. This weight loss is attributed to the loss of absorbed moisture. The second step of degradation at ~280 °C corresponds to the degradation of the aromatic sulfonyl groups, whereas the degradation in the third step is due to the decomposition of the main chain. The stability of the composite membranes was increased by an increase in the STA content. From the thermograms, one can observe that the percentage of weight loss in the second step decreased with an increase in the STA content. This decreased weight loss occurs despite the fact that the amount of sulfonic acid group decreases with increasing STA content. This observation further confirms the successful incorporation of STA into the polymer matrix.

HPA extraction

The extraction of HPA is an important parameter for illustrating the efficiency of the composite membranes. The amount of HPA extracted from the composite membranes was determined using a ultraviolet–visible spectrophotometer. The decrease in HPA extraction with increasing STA content is shown in Figure 7. In all, 18% of HPA leached out from the SPAES/STA-10 composite membrane, whereas only 10% of HPA leached out from the SPAES/STA-40 membrane. The proper stoichiometry may account for the low HPA extraction from the composite membranes.¹³ The extraction of HPA from the composite membranes decreases with an increase in HPA content in the order of SPAES/STA-10 > SPAES/STA-20 > SPAES/STA-30 > SPAES/STA-40.

Proton conductivity

Generally, the proton conductivity directly depends on the water uptake and IEC of the polymer.²³ The performance and the efficiency of the fuel cell depends on the proton conductivity.²⁴ The water uptake of the sulfonated polymers have a profound effect on proton conductivity and mechanical properties.²⁵ A high water retention capacity leads to higher proton conductivity. However, high water retention causes swelling and decreases the mechanical properties because of undesirable dimensional changes. The conductivities of the SPAES/STA composite membranes with increasing temperature were determined. Figure 8 shows that the proton conductivity of the composite membranes increased as SPAES/STA-0 < SPAES/STA-10 < SPAES/STA-20 < SPAES/STA-30 < SPAES/STA-40. Though there was a decrease in the IEC, an increase in the proton conductivities of

Figure 6 Thermogravimetric analyses thermograms of the composite membranes. a, SPAES/STA-0; b, SPAES/STA-20; c, SPAES/STA-40.

Figure 7 HPA extraction of the composite membranes.

Figure 8 Proton conductivity of the composite membranes. —○—, SPAES/STA-0; —●—, SPAES/STA-10; —▲—, SPAES/STA-20; —■—, SPAES/STA-30; —◆—, SPAES/STA-40.

Table 2 Hydrolytic stability of the composite membranes

Polymer code	UTM method			Soaking and folding method (h)
	Film pre-treatment ^a	Tensile strength (MPa)	Young's modulus (GPa)	
SPAES/STA-0	Before	50.9	1.36	200
	After	20.4	0.54	
SPAES/STA-10	Before	53.1	1.41	215
	After	23.1	0.60	
SPAES/STA-20	Before	57.4	1.49	235
	After	28.0	0.72	
SPAES/STA-30	Before	62.1	1.58	260
	After	32.1	0.79	
SPAES/STA-40	Before	65.4	1.71	> 275
	After	38.5	0.87	

Abbreviation: UTM, universal testing machine.

^aBefore: dried in vacuum oven at 1000 °C for 24 h.

After: immersed in hot water at 80 °C for 1 h.

the composite membranes may be due to the following factors. The acidity of the sulfonic acid group increased with the incorporation of STA. Because the composite membranes showed a negligible STA extraction, most of the STA was retained in the polymer and this increases the efficiency of the membrane. The absorbed water molecules in the membranes are held by the strong hydrogen bonds among STA and the hydrogen bonds between the sulfonic acid group of SPAES and STA. These retained water molecules results in the increase of proton conductivity of the composite membranes. The proton conductivity increases when the operating temperature is increased (~90 °C). This increase occurs because, with greater water retention at 90 °C, the formation of the hydrophilic domain is improved, which enhances the proton conductivity. When the temperature reached 90 °C, the mobility of water, reorientation of the polymer and flexibility of the polymer were increased. The proton transfer is facilitated by the presence of water molecules. Because the amount of water molecules trapped in the composite membranes increases with STA content, the proton conductivity is increased at elevated temperature.

Hydrolytic stability

The longevity of the electrolyte membranes in fuel cells enhances hydrolytic stability. In this study, several approaches were adopted for the purpose of increasing the hydrolytic stability of the sulfonated polymers. SPAES/STA blends were prepared and their corresponding hydrolytic stability was evaluated using two different methods. The first method is the physical verification of the membrane after a stipulated time in boiling water by folding and unfolding the membrane. The time at which the membrane breaks while folding is noted as the time of disintegration. In the second method, the membrane is soaked for a stipulated time in hot water and tested to find the tensile strength. These results, summarized in Table 2, show that the hydrolytic stability of the composite membranes increased in the following manner: SPAES/STA-0 < SPAES/STA-10 < SPAES/STA-20 < SPAES/STA-30 < SPAES/STA-40. In both of the methods, the hydrolytic stability of the composite membranes is better than the parent membrane.

CONCLUSIONS

Composite membranes from SPAES and STA were synthesized by varying the STA and SPAES contents. The successful incorporation of

STA was confirmed using FT-IR and thermogravimetric analysis. The IEC values decreased as SPAES/STA-0 > SPAES/STA-10 > SPAES/STA-20 > SPAES/STA-30 > SPAES/STA-40. This is attributed to a decrease in sulfonic acid groups with increasing STA content. The water uptake follows the same trend as the IEC. The composite membranes exhibited higher thermal stability than the parent SPAES membrane. The proton conductivities of the composite membranes are higher than those of the parent membranes. Though the IEC and the water uptake of the composite membranes decreases with increasing STA content, the proton conductivities and hydrolytic stabilities increased with increasing STA content. The retention of trapped water, even at high temperature, by the rigid aromatic groups and the strong hydrogen bonds of STA lead to high proton conductivity and hydrolytic stability. Although the extraction of HPA from the composite membranes decreased with an increase in HPA content, the proton conductivities of the composite membranes increased. The highest proton conductivity of 0.109 S cm⁻¹ was obtained at 30 °C for SPAES/STA-40. Furthermore, the mechanical properties of the composite membranes were improved by increasing the HPA content. The water uptake of the composite membranes decreases with an increase in HPA content, which leads to reduced polymer swelling, which accounts for the higher hydrolytic stability.

ACKNOWLEDGEMENTS

We are thankful to the Director of the CLRI for the support provided in performing this research work. We are also thankful to Dr S Pitchumani, Central Electro-Chemical Research Institute, CSIR Madras Complex for the proton conductivity experiments.

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