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PAPER

Novel Fuel Cell Membrane with High Efficiency†

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5 New class of polymer electrolyte membranes containing azo based ionic diol (30, 40 and 50 mol %) was prepared to use in the fuel cell. Proton conductivity, hydrolytic stability, water uptake capacity, swelling behaviour and ion-exchange capacity measurement data indicated its suitability for use as proton exchange electrolyte membrane in fuel cell. For example, the membrane containing 30, 40 and 50 mol % of azo based ionic monomers exhibit fairly good proton conductivity of 0.073 S cm⁻¹, 0.075 S cm⁻¹ and 10 0.079 S cm⁻¹ respectively at 30 °C. Moreover, the prepared membranes show phase separated morphology and exhibit high thermal stability up to 460 °C: important parameter for successful fuel cell design. Two types of azo based sulfonated poly(arylene ether sulfone) (SPAES) such as SPAES-30 and SPAES-50 membrane electrode assembly have been successfully fabricated that yielded good fuel cell performance in the whole range of current density.

15 Introduction

The majority of the energy needs have been provided by combustion of fossil fuels. Due to depleting natural resources and hiking petroleum prices, the search for alternative fuel got intensified. Fuel cells are reliable power generation devices for 20 vehicles, transportation and portable devices to save significant amount of energy and reduce the emission of non-greenhouse gases.^{1,2} Fuel cell systems have the ability to solve the most challenging problems associated with current battery systems.³ Unlike the conventional power generation technique, fuel cell 25 works without combustion and environmental side effects. It produces direct current and acts like continuously fuelled batteries. Recent studies have been focussed on non-fluorinated hydrocarbon-based polymer electrolyte membranes and composite^{4,5} membranes due to the loss of 30 stability and conductivity at high temperatures in perfluorosulfonic acid membranes. High temperature operation provides the following advantages in fuel cells.

- i) Simplification of the cooling system.
- ii) Enhanced proton conductivity.
- 35 iii) Improved tolerance of the electrodes to carbon monoxide.
- iv) Better kinetics of methanol oxidation.
- v) Potential use of cogeneration heat.

40 Proton Exchange Membrane Fuel Cell (PEMFC) is one of the best types of fuel cells for vehicular power source to ultimately replace the fuel and diesel internal combustion engines. The interest in fuel cell is basically due to their ability to continuously convert chemical energy in to electrical energy with high 45 efficiency and low emission of pollutants.⁶⁻⁹ The proton exchange membrane is a key component of the PEMFCs that usually acts

as an electrolyte to form ionic pathways for the protons to pass from anode to cathode. A fuel cell membrane must have thermal, chemical and mechanical stability along with good proton 50 conductivity. The performance of an electrolyte membrane was controlled by various physical parameters like ion-exchange capacity, water uptake, swelling behaviour and proton conductivity. The stability and proton conductivity of the electrolyte membranes are related to the polymer backbone and 55 its acid moiety respectively.

Perfluorinated ionomers have an outstanding physical and chemical stability and show an excellent performance when applied in fuel cells, especially in H₂ fuel cells. Nafion® is the commercially available standard polymer electrolyte membrane 60 used in PEMFCs due to their excellent mechanical and chemical stabilities.^{10,11} It is quite resistant to chemical attack and has a highly phase separated morphology that imparts excellent proton conductivity with moderate water uptakes.¹²⁻¹⁴ However, the limitations of these membranes are their high cost and production 65 process, which may include high toxic and environmental-unfriendly intermediates.¹⁵ Nafion® exhibits high methanol permeability and low conductivity at low humidity or high operating temperature, which restrict its commercialization.^{16,17} These drawbacks are the main reasons for the extensive research 70 to develop alternative proton exchange membranes for fuel cell.¹⁸⁻²¹

Sulfonated polyimides,²²⁻²⁴ sulfonated polysulfones,^{25,26} sulfonated poly(ether ether ketone)s,²⁷⁻²⁹ sulfonated poly(arylene ether sulfone)s,³⁰⁻³² sulfonated polystyrenes,^{33,34} and 75 polybenzimidazoles^{35,36} have been studied for fuel cell membranes because of their good stability, conductivity and processability. Among these polymers, sulfonated poly(arylene ether sulfone)s have been a centre of attention of recent studies in search of replacement for Nafion®. Although improvements have 80 been achieved with these types of polymers, the proton

conductivity at elevated temperatures is still un-satisfactory because of the lack of water retention at temperatures much above 100 °C.³²

5 The post sulfonation process of the high performance materials such as polysulfones, poly ether ether ketones etc., have suggested that these materials are unable to form defined hydrophilic domains. Due to the rigid polymeric backbones, it prevents the formation of ionic clusters. So the introduction of
10 ionic groups in side chain polymer via direct copolymerization method improves the formation of ionic cluster, ion-exchange capacity and proton conductivity. Another advantage of this method is that it allows close control of sulfonation and the polymer structure.

15 Several types of poly(arylene ether sulfone)s (PAES) are reported in the literature, where the anionomers located in the main chain³⁷⁻³⁹ and side chain⁴⁰⁻⁴² of the aromatic ring. Most of the arylene polymers are functionalized by sulfonating the base
20 polymer with sulfonating agents like conc. sulfuric acid, oleum, chlorosulfonic acid etc. The process of post sulfonation suffers some disadvantages, which may be due to its high degree of sulfonation, degradation and cross-linking by reaction sensitivity.⁴³ If the post sulfonation takes place at the active sites
25 of the benzene ring, it may lead to the risk of desulfonation under fuel cell conditions. Based on the above drawbacks, new monomers of novel architecture are synthesized. In this work, for the first time we report the syntheses of azo based SPAES membranes for fuel cell applications. The physical and chemical
30 properties of these membranes were characterized using various instrumentation techniques in order to evaluate the suitability of these membranes for fuel cells.

Experimental

Materials

4,4'-Dichlorodiphenylsulfone (DCDPS), resorcinol and *N,N'*-dimethylacetamide (DMAc, 99.8 %) were purchased from
40 Aldrich Co., USA. Sulfanilic acid, sodium nitrite, sodium carbonate, 4,4'-bisphenol-A (BP-A), potassium carbonate, *N,N'*-dimethylformamide, methanol and toluene were purchased from Sisco Research Laboratory Private Ltd., Mumbai, India. *N*-methyl-2-pyrrolidone was purchased from S. D. Fine Chem. Ltd.,
45 Mumbai, India. DCDPS and BP-A were dried at 80 °C under vacuum for 16 h before the usage. All other chemicals were used as received.

Monomer synthesis

50 The azo based ionic diol having sulfonic acid group, (E)-4-((2, 4-dihydroxyphenyl)diazanyl)benzene sulfonic acid was synthesized by diazotization reaction followed by coupling reaction. The reaction scheme for the synthesis of azo based diol is shown in
55 ESI Scheme S1. In a 250 mL beaker, 75 g of ice-water mixture and 10 mL of conc. HCl were taken and stirred at 0-5 °C. An amount of 8.65 g of sulfanilic acid (50 mmol) in 90 mL of 2.5 % sodium carbonate solution was added to the beaker followed by the addition of 3.45 g of saturated solution of sodium nitrite (50

60 mmol). A powdery white precipitate of diazonium salt was obtained within few minutes. An amount of 4.40 g of resorcinol (40 mmol) in 60 mL of water was slowly added to the beaker through addition funnel and stirred well for 30 min at 0-5 °C. The orange coloured precipitate was collected by filtration, washed
65 thoroughly with ice-cold water and recrystallized from deionized water. The product was dried at 60 °C under vacuum for 12 h.

Polymerization

70 A typical polymerization procedure for the synthesis of SPAES-50 is as follows; 4,4'-Dichlorodiphenylsulfone (14.35 g, 50 mmol), bisphenol-A (5.70 g, 25 mmol) and azo based monomer (7.38 g, 25 mmol) were placed in a 250 mL three-necked RB flask equipped with a magnetic stirrer, Dean-Stark trap and
75 nitrogen inlet. A volume of 60 mL of DMAc was added and stirred well until all the monomers were dissolved. An amount of 13.8 g of anhydrous potassium carbonate (100 mmol) and 30 mL of toluene were added and refluxed at 150 °C for 5 h. Following this step, the temperature was slowly raised to 180 °C after
80 controlled removal of toluene from the reaction mixture. The polymerization reaction was continued at 180 °C for 18 h. The viscous solution was cooled to 25 °C and diluted with DMF to allow easier filtering. Then, the solution was filtered using 100 µm pore size filter paper to remove most of the potassium salts.
85 The polymer solution was slowly added to a beaker containing an excess of methanol. The precipitated azo polymer was washed several times with ethanol and then dried at 80 °C under vacuum for 24 h.

Membrane preparation

The SPAES copolymer of 10 wt % was dissolved in DMAc at 25 °C under constant stirring. After the complete dissolution of SPAES, the viscous solution was cast onto a flat glass plate. The
95 cast membranes were dried at 60 °C for 12 h, 90 °C for 10 h and 140 °C for 6 h. Following this step, the resulting membranes were soaked in deionized water for 24 h to release the membranes from the glass plates. The obtained membranes were thoroughly washed with deionized water and finally dried at 80 °C under
100 vacuum for 24 h.

Measurements

For the Fourier Transform Infrared Spectra (FT-IR) analysis, the
105 samples were first dried at 100 °C under vacuum for 6 h. The spectrum was collected using ABB MB3000 FT-IR spectrophotometer. High Performance Liquid Chromatography (HPLC) analysis was performed using a LC-10AT-VP, Shimadzu, Japan. Surface morphology was analyzed using
110 scanning electron microscope (SEM, Hitachi-S3400N). For SEM analysis, the samples were cut into sufficient size and sputter coated with gold to make electro conductive. Then the sample was analyzed under vacuum at an accelerating voltage of 10.0 KV. Thermogravimetric analyses of the membranes were carried
115 out using a Thermogravimetric Analyzer (Q 50, TA Instruments, USA) at a heating rate of 20 °C min⁻¹ in nitrogen atmosphere. Intrinsic viscosity measurements were obtained in *N*-methyl-2-

pyrrolidone at 25 °C using a capillary viscometer, Schott Geräte, West Germany. GPC analysis was done in DMF solvent. HR-TEM images were carried out on FET TECHNO G² 30 (300 KV) instrument.

The concentration of the ion conducting units is generally denoted as the molar equivalents of ion conductor per mass of dry sample and is expressed as Ion Exchange Capacity (IEC). The IEC of the membranes was measured using the titration method. The polymer membranes were soaked in 1.0 M HCl for 10 h to regenerate the protons from the salt form. All the membranes were thoroughly washed with deionized water for several times and then soaked in 0.1 M NaCl solution for 16 h. The protons released due to the exchange reaction with Na⁺ ions were titrated against 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC was determined from equation 1.

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

where

V is the volume of NaOH consumed

N_{NaOH} is the normality of NaOH

meq. is milliequivalent

For the water uptake and swelling ratio studies, the acidified membranes were dried at 120 °C until constant weights and lengths were achieved, which are recorded as W_{dry} and L_{dry} respectively. Then, the dried membranes were immersed into deionized water. The water attached to the surface was quickly swabbed with tissue paper before measurement. The weight and length were measured several times until constant measurements were achieved, which are denoted as W_{wet} and L_{wet} respectively. The percentage water uptake of the membrane was calculated using equation 2.

$$\% \text{ Water uptake} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100 \quad (2)$$

The swelling ratio was defined as equation 3.

$$\% \text{ Swelling ratio} = (L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}} \times 100 \quad (3)$$

The proton conductivity measurements were performed in a two-probe cell using AC impedance spectroscopic technique. The AC impedance spectra of the membranes were recorded in the frequency range of 1.0 MHz - 10.0 Hz using an Autolab PGSTAT 30. The detailed procedure for conductivity measurements was reported in our paper.³² The measurements were taken in the temperature range of 30 °C - 130 °C. The tensile strength and Young's modulus of the completely hydrated SPAES membranes were measured using Universal Testing Machine (UTM), Instron, USA. Samples having a length of 50 mm and a width of 20 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 carried out and taken the average values for the determination of tensile strength and Young's modulus.

A 15 weight % of teflonized Toray-TGP-H-120 carbon paper of 0.37 mm thickness was used as the backing layer. To prepare the gas-diffusion layer (GDL), Vulcan XC-72R was suspended in

cyclohexane and agitated in an ultrasonic water bath for 30 min. 15 weight % polytetrafluoroethylene (PTFE) suspension in 2 ml ammonia was added to this solution with continuous agitation to form slurry that was coated onto the backing layer uniformly until required loading of 1.5 mg/cm² carbon was obtained. The obtained GDL was sintered in a muffle furnace at 350 °C for 30 min. Carbon supported platinum was used as catalyst for both cathode and anode. The loading of the catalyst layer on both the anode and cathode was kept at 0.5 mg/cm². The active area for the PEMFC was 4.0 cm². The MEA of the pristine and composite membrane was prepared by sandwiching the membrane between the two electrodes followed by its hot-pressing at 130 °C for 3 min at a pressure of 20 kg/cm². The MEA was evaluated using a conventional fuel cell fixture with parallel serpentine flow-field machined on graphite plates. The cells were tested at 60 °C under 100% humidified condition with hydrogen at a flow rate of 100 mL/min at the anode and oxygen at a flow rate of 150 mL/min at the cathode, respectively. Measurements for cell potentials with varying current densities were conducted galvanostatically using a Fuel Cell Test Station (Model- LCN4-25-24/LCN 50-24) procured from Bitrode Instruments (USA).

Results and discussion

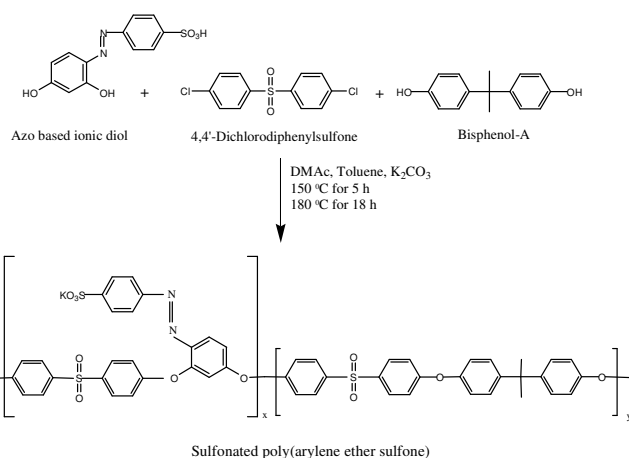
Synthesis of azo based sulfonated poly(arylene ether sulfone)s

A series of SPAES copolymer membranes were synthesised by aromatic nucleophilic polycondensation reaction. The polymer code, mole ratio of monomers such as bisphenol-A and azo based ionic diol used for the synthesis of SPAES and their physical properties are given in Table 1. The reaction was carried out in the presence of potassium carbonate using *N,N*-Dimethylacetamide (DMAc) as a solvent (Scheme 1). The resulting polymers had intrinsic viscosity in the range between 1.41 and 1.54 dL g⁻¹. Gel Permeation Chromatography (GPC) experiments (ESI, Fig. S4) indicated the weight average molecular weight (Mw) and polydispersity index (PDI) of SPAES-30 to be 10640 Daltons and 1.41 respectively while Mw and PDI values for SPAES-40 were 6321 Daltons and 1.31 respectively.

Table 1 Mole ratio and physical properties of SPAES copolymers

Polymer code	Mole ratio of BP-A/ionic diol in copolymers	$\eta_{\text{int}}^{\text{a}}$ (dL g ⁻¹)	Tensile strength (MPa)	Young's modulus (MPa)	Activation Energy (kJ.mol ⁻¹)
SPAES-30	1 : 0.6	1.41	43	513	7.48
SPAES-40	1 : 0.8	1.46	40	468	7.33
SPAES-50	1 : 1.0	1.54	33	402	7.01

^a Intrinsic viscosity measured at a concentration of 1.0 g dL⁻¹ in NMP at 25 °C.



Scheme 1 Synthesis of azo based SPAES.

Spectral analyses

High performance liquid chromatography (HPLC) analysis confirms the absence of starting material in azo based ionic diol. The chromatograms of the starting material and azo based ionic diol are given in Fig. 1. The reverse-phase HPLC analysis performed by using the mobile phase in the proportion of 70:30 methanol and water, pH 2.0 adjusted with formic acid. The flow rate was set to 0.75 mL min^{-1} . The HPLC analysis was carried out by LC-10AT-VP, with Photo Diode Array (PDA) detector, in which we can collect the chromatogram at different wavelength.

A volume of $20 \mu\text{L}$ (0.10 mg mL^{-1} concentration) of both the starting material and product in methanol medium was injected through a rhodine setup. The λ_{max} of resorcinol was found to be 270 nm , whereas the product at 350 nm . The chromatograms were collected at a wavelength of 350 nm for the azo compound and 270 nm for resorcinol. The retention time of resorcinol was obtained at 2.91 min and the product at 3.96 min . In ESI Fig. S1, the expand view of chromatogram of the azo based ionic diol at a wavelength of 270 nm with the retention time of 2.91 min clearly shows the absence of the starting material.

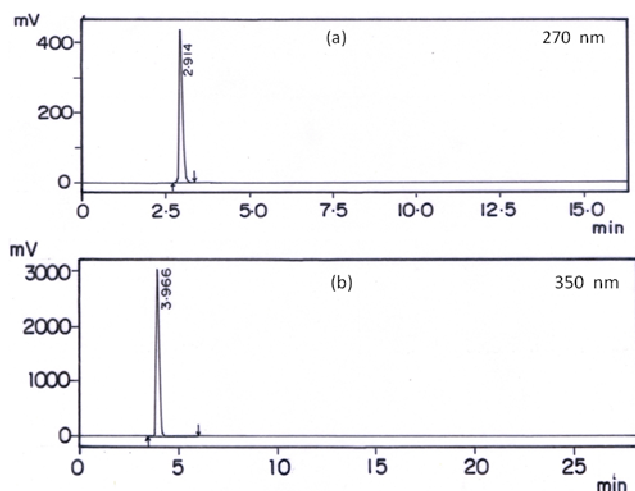


Fig. 1 HPLC Chromatograms of starting material (a) and azo based ionic diol (b).

The FT-IR spectrum of the azo based ionic diol is given in ESI Fig. S2. A broad band appeared at 3475 cm^{-1} is attributed to the presence of hydroxyl groups. The aromatic C-C band was appeared at 1120 cm^{-1} . The peaks at 1166 and 1033 cm^{-1} are obtained because of the stretching vibration ($\text{O}=\text{S}=\text{O}$) of sulfonate salt. The FT-IR spectrum of the azo based SPAES-50 copolymers is shown in Fig. 2. The peaks at 1585 cm^{-1} and 1488 cm^{-1} are attributed to the vibrations of the aromatic ring skeleton. The symmetric stretching band of the sulfone group was appeared at 1153 cm^{-1} and 1012 cm^{-1} . The peak at 1242 cm^{-1} proves the aromatic ether linkage of the SPAES. The aromatic C-N stretching vibration is observed around 1325 cm^{-1} .

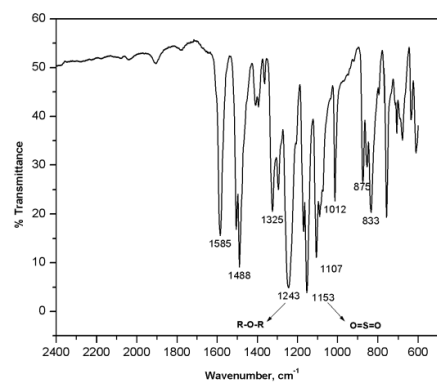


Fig. 2 FT-IR spectrum of azo based SPAES-50 copolymer.

Proton NMR analysis was performed for the azo based ionic diol and the polymer (SPAES-50) using $\text{DMSO-}d_6$ as solvent. The proton NMR spectra of the azo based ionic monomer and the SPAES polymer are shown in Fig. 3. In the azo based monomer, the resonance signal appears at 8.06 to 6.90 ppm are due to the aromatic protons and the sulfonic acid proton appears at 2.00 ppm (see Fig. 3a). The polymer (SPAES-50) shows the resonance signals appearing at 8.10 to 7.00 ppm for aromatic protons. The methyl protons in SPAES-50 appear at 1.65 ppm confirming the formation of a polymer.^{18,44}

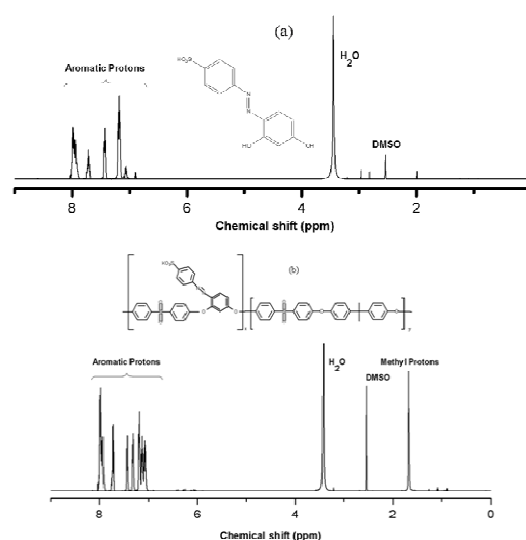


Fig. 3 ^1H NMR spectra of azo monomer (a) and SPAES-50 copolymers (b).

Ion exchange capacity

Ion exchange capacity (IEC) is an essential parameter for the evaluation of a polymer electrolyte membrane as it influences the water uptake and proton conductivity. The IEC of the polymer is directly dependent on the amount of sulfonic acid substituted in the polymer. Generally the proton conductivity and the water uptake of the final membrane directly depend on the amount of sulfonic acid group and IEC of the polymer. But the sulfonic acid groups not only make the polymer proton conducting but also make it hydrophilic. The IEC values of SPAES copolymers are given in Table 2.

Table 2 The IEC, water uptake and swelling ratio of SPAES copolymers

Polymer code	IEC (meq. g ⁻¹)	Water uptake (%)		Swelling ratio (%)	
		30 °C	90 °C	30 °C	90 °C
SPAES - 30	1.63	26.2	33.6	4.75	6.06
SPAES - 40	1.69	28.0	38.4	5.52	6.63
SPAES - 50	1.86	35.1	45.6	6.69	8.07

As the proportion of azo monomer having ionic group in SPAES membranes is increased, the IEC also increased. It can be seen that the order increased in the following manner: SPAES-30 < SPAES-40 < SPAES-50. The IEC value of the membranes clearly shows that the sulfonated monomers were well incorporated into the copolymers.

Water uptake and swelling ratio

Water uptake capacity and swelling behaviour are very important parameters in PEMFC applications, because the proton conductivity and hydrolytic stability of polymer electrolyte membranes are strongly related to the presence of water. Polymer electrolyte membrane with good water management ability would be anticipated for fuel cell application. In this work, the water uptake capacity and swelling ratio of the membranes were analyzed at temperatures between 30 °C and 90 °C. The influence of IEC on the water uptake of SPAES membranes is depicted in ESI Fig. S3. Here, the water uptake follows the same trend as IEC and the values are given in Table 2. At 90 °C, SPAES copolymers showed moderate water uptake and swelling. This may be attributed to the construction of large and continuous ion linkage in the sulfonated polymers. Water uptake increased with sulfonate content due to the strong hydrophilicity of the sulfonic acid group. Also bisphenol structure had a remarkable influence on water uptake and swelling ratio of the membranes.

Thermal and hydrolytic stability

The thermal stability of the SPAES membranes was determined using TGA measurements and the thermograms are shown in Fig. 4. All membranes showed a three step degradation pattern. The first step of mass loss (5 %) up to 200 °C in SPAES copolymers is due to the loss of physically and chemically bound water. The second step of degradation was found in the range of 200-460 °C which corresponds to the splitting of aromatic sulfonyl groups as well as the degradation of azo groups. The third weight loss

occurs at about 460 °C was due to the decomposition of the polymer backbone.⁴⁵⁻⁴⁶ SPAES-50 shows higher stability than SPAES-30 and SPAES-40. In general, the azo polymers are found to exhibit better thermal stability, the rigidity being enhanced by the presence of azo groups. These membranes showed slight differences in thermal stability according to their mole ratio.

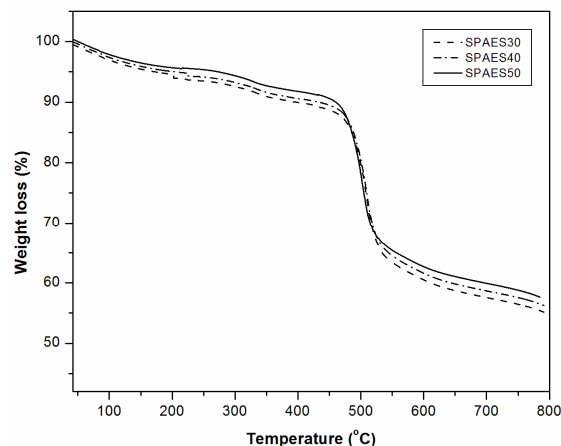


Fig. 4 The TGA thermograms of SPAES copolymers.

Azo based SPAES membranes had reasonably good physical properties. It is very important for polymer electrolyte membrane to have good mechanical properties to withstand high temperature, high pressure fabrication process for membrane electrode assembly and the extreme conditions of a fuel cell. The mechanical properties of dry SPAES membranes are summarised in Table 1. All membranes exhibit tensile strength in the range from 33.6 to 43.3 MPa and modulus from 402 to 513 MPa which are flexible for the usage of polymer electrolyte membranes. An increase in sulfonic acid content in to the polymer matrix, resulted in the reduction of tensile strength. From the mechanical testing, it can be concluded that the side chain substituted SPAES membranes are flexible for fuel cell applications.

Proton conductivity

For good proton conductivity, solid electrolyte membranes should have fixed charged sites surrounded by water molecules which facilitate the transport of protons.⁴⁷ The SPAES membrane has high proton conductivity because the sulfonic acid groups have covalent bonding (S-O) and intermolecular hydrogen bonding. So the principle of proton conduction is Grotthuss mechanism, when the protons are transferred by forming and breaking hydrogen bonds with proton accepting media such as water or sulphonic acid.⁴⁸ Several researchers have reported on different kinds of proton conducting materials as the alternative to the Nafion[®] membranes.⁴⁹ The water uptake capacity of the sulfonated polymers have a profound effect on proton conductivity and mechanical properties.⁵⁰ For conductivity experiments, all the membranes were initially immersed in deionized water for 24 h at 25 °C to hydrate. The proton conductivity of the membranes based on the monomer which have more sulfonic acid content possess higher conductivity. The conductivities of the SPAES membranes with increasing temperature from 30 °C to 130 °C

were determined and found the values markedly increased in the order of SPAES-30 < SPAES-40 < SPAES-50. The increase in proton conductivity of the membranes is due to more water retention and increase in the formation of the ionic clusters.

Fig. 5 shows an Arrhenius plots of the proton conductivity as a function of temperature for SPAES membranes and the E_a values are reported in Table 4.2. The activation energy of the membranes were decreased in the order of SPAES-30 > SPAES-40 > SPAES-50. The increase in percentage water uptake of the

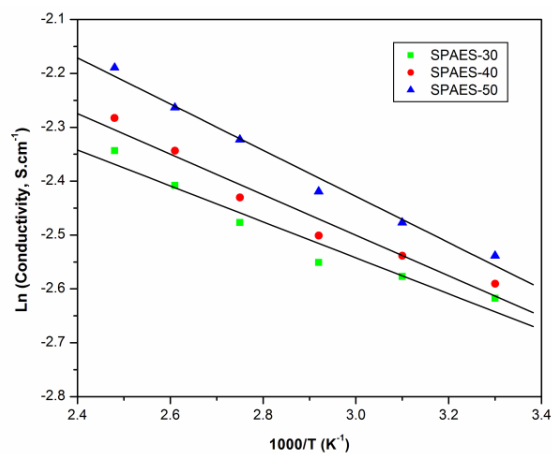


Fig. 5 Arrhenius plots of proton conductivity for SPAES membranes.

SPAES membranes lead to lowering its activation energy as consequence of increase in proton conductivity. A similar trend of increasing proton conductivity with increase in ionic content was reported by Pei *et al.*⁵¹ Membranes having ionic groups in its side chain exhibit excellent proton conductivity. Table 3 describes the compilation of some of the reported values of sulfonated polymers having side chain ionic groups.

Table 3 IEC and proton conductivity values of sulfonated polymers having ionic groups as side chains

Membrane type	IEC (meq. g ⁻¹)	Proton conductivity (S/cm)	Reference
Cardo poly(aryl ether sulfone)s with pendant – OH groups	1.41	0.06 (20 °C)	52
SPES containing hexabenzocoronene	1.61	0.11 (80 °C)	53
SPEScontaining DHTPE ^a	1.68	0.10 (80 °C)	54
Sulfonated poly(phenylene oxide)	1.62	0.07 (25 °C)	55
Concentrated SPES	1.51	0.06 (20 °C)	56
SPAES having azo based ionic diols	1.86	0.08 (30 °C)	This work

^aDHTPE – (4,4-(2,2-diphenylethylidene)bisphenol).

It can be seen from the above compilation that the IEC and proton conductivity of the azo based SPAES membranes are good and

can be considered for PEMFC applications.

Electrochemical study

The SPAES-30 and SPAES-50 membranes were taken for MEA studies. Fig. 6 shows the cell polarization of MEA assembled with the synthesised SPAES membranes as electrolyte at 60 °C and 100 % RH. The best performance under these conditions was obtained for SPAES-50 membrane, which produced a peak power density of 496 mW/cm² at a load current density of 1500 mA/cm² as compared to the SPAES-30 membrane with 465 mW/cm² at 1500 mA/cm². Recently, Lim *et al* synthesized SPES containing DHTPE and achieved a maximum power density of 420 mW/cm².⁵⁷ They also compared their values with Nafion[®] 211, where it exhibits 450 mW/cm². Sahu *et al* reported that PEMFC with Nafion[®] 1135 membrane produced a peak power density of 550 mW/cm² at 60 °C and 100 % RH.⁵⁸ The cell polarization curve of azo based SPAES membrane exhibits good performance in PEMFC applications.

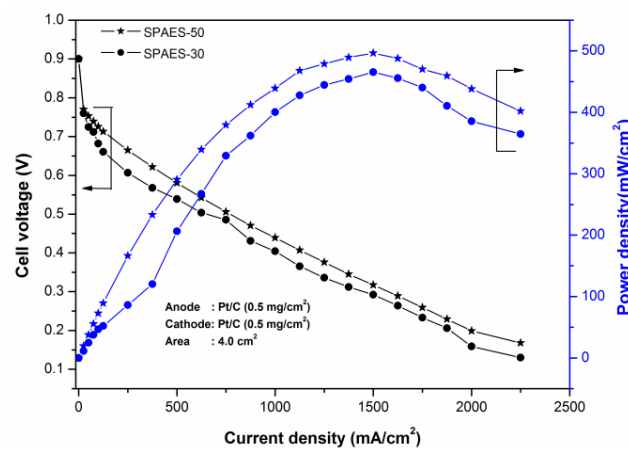


Fig. 6 The electrochemical single cell performance of SPAES-50 membrane at 60 °C and 100 % RH.

Conclusions

A novel azo based diol, (E)-4-((2,4-dihydroxyphenyl) diazenyl) benzene sulfonic acid was successfully synthesised by diazotisation reaction followed by coupling reaction. Sulfonated poly(arylene ether sulfone)s with different mole ratio of hydrophilic groups were prepared by changing the mole ratio of azo based ionic diol and bisphenol-A. These are the new type of proton exchange membranes having azo and sulfonic acid groups as side chains in SPAES. The obtained polymers had intrinsic viscosity of 1.41-1.54 dL/g. With increase in sulfonic acid content in to the polymer matrix, water uptake increased from 26.2 to 35.1 % at 30 °C and 33.6 to 45.6% at 90 °C. All membranes exhibit excellent thermal stability with 10 % weight loss observed up to 460 °C. A single cell using SPAES-50 membrane as an electrolyte produced a maximum power density of 496 mW/cm² in H₂/O₂ at 60 °C under 100 % RH. The high proton conductivity and thermal stability of the azo based SPAES membranes meet the requirements of good proton exchange membranes for PEMFC applications.

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† Electronic Supplementary Information (ESI) available: [Synthetic scheme for azo based diol, HPLC Chromatogram of the expand region of azo based ionic diol, FT-IR spectrum of the azo based monomer and the influence of IEC on the water uptake of SPAES membranes were present].

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Graphical Abstract

Novel Fuel Cell Membrane with High Efficiency

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Novel polymer containing azo based ionic diol have been successfully fabricated as electrolyte membranes to yield good fuel cell performance in the whole range of current density.

