DEVELOPMENT AND CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE - IMIDAZOLIUM FUNCTIONALIZED POLYSULFONE BLEND ANION EXCHANGE MEMBRANE

S. VELU, K. RAMBABU*

Chemical Engineering Division, School of Mechanical and Building Sciences, Vellore
Institute of Technology University, Vellore 632014, India
*Corresponding Author: rambabu.k@vit.ac.in

Abstract

Anion exchange membrane (AEM) is one of the core components of an alkaline fuel cell influencing the fuel cell's performance, durability and stability. Out of the many anion exchange membranes reported so far, imidazolium functionalized polysulfone (PSf-ImOH) membrane has been identified to have high hydroxide ionic conductivity, reaching up to 50 mS cm^{-1} at 20°C. However, at high levels of ion exchange capacity, the membrane's water uptake and swelling ratio increases significantly with temperature thus destabilizing it and making it unfit for potential use in high temperature alkaline fuel cells. This limitation of PSf-ImOH membranes has been overcome by blending it with polyvinylidene fluoride (PVDF) polymer, which is a thermally stable and highly hydrophobic polymer. PSf-ImOH membrane with a high degree of chloromethylation (180%) was synthesized and blended with PVDF at different weight ratios (PVDF / PSf-ImOH: 30/70, 50/50 and 70/30) to create a series of novel anion exchange membranes. The prepared membranes were characterized to study their structure, water uptake, swelling ratio, solubility in low boiling water soluble solvents, thermal stability, ion exchange capacity (IEC) and ionic conductivity (IC) at different temperatures. The 70% PVDF blend membrane demonstrated the better performance in terms of IEC, IC and water uptake properties compared to other membranes. Comparative studies on the water uptake and IC variation between the 70% PVDF blend membrane and pure PSf-ImOH membrane (having the same IEC as that of the blend membrane), clearly indicated the superiority and the promising use of the blend membrane in alkaline fuel cell especially for high temperature working condition.

Keywords: Blended membranes, Imidazolium functionalized polysulfone, Poly-
          vinylidene fluoride, Anion exchange membrane, Alkaline fuel cell.

Nomenclatures

C_{HCl}	Concentration of HCl solution, M
D_{dry}	Average dimension of the dry membrane sample, g
D_{dry1}	Length of the dry membrane sample, mm
D_{dry2}	Width of the dry membrane sample, mm
D_{wet}	Average dimension of the wet membrane sample, g
D_{wet1}	Length of the wet membrane sample, mm
D_{wet2}	Width of the wet membrane sample, mm
SR	Swelling ratio of the membrane sample, %
V_b	Volume of NaOH consumed for blank solution titration, mL
V_s	Volume of NaOH consumed for membrane sample titration, mL
WU	Water uptake of the membrane sample, %
W_{wet}	Weight of the wet membrane sample, g
W_{dry}	Weight of the dry membrane sample, g

1. Introduction

Growing shortage of fossil fuels and the limitations on the current fossil fuel processing technologies has triggered the search for a clean and efficient fuel technology. Fuel cells seem to be a promising technology to overcome the above limitations and to meet the current demands of clean fuel processing. Recent decades has seen increased research focus on the advancement of alkaline fuel cell (AFC) compared to proton exchange membrane fuel cell (PEMFC). Usage of non-noble metal electrodes [1, 2], faster reduction kinetics at the electrodes [3, 4] and relatively low operating temperatures (23-70°C) [3] are some of the salient advantages of AFC over PEMFC. Usage of the solid polymer anion exchange membrane (AEM) as the conducting medium has overcome the limitations of the previously used liquid electrolyte (potassium hydroxide) in the AFC [4-6]. This has led to intensive research for the development of solid polymer anion exchange membranes.

Of the many desired properties for the solid polymer AEM, ionic conductivity (IC) and the stability of the membrane (chemical, mechanical and thermal) are very important features affecting the performance of the membrane in the fuel cell applications [7, 8] . A high IC value for the AEM can be achieved by increasing the amount of ion carrier groups in unit mass of the dry membrane. However, the high IC value is generally associated with poor membrane mechanical stability resulted from the excessive water uptake by the ion carrier groups [9]. Hence development of a thermo-mechanically stable AEM with high IC value is highly desirable in the development of AEM. AEMs with high IC and desired stability were initially obtained by quarternization of solid hydrophilic polymers for low temperature applications [10, 11].

The polymers were usually functionalized by introducing the hydroxide carrier group into them via 3 step process - chloromethylation, quarternization and alkalization to obtain the hydroxide functionalized AEM. Aromatic ring polymers were usually selected for the preparation of stable and high IC AEMs. Membranes of poly(ether-imide) [12], poly(ether ether ketone) [13], polysulfone [14-20], cardo polyether ketone [21], cardo polyethersulfone [22, 23], polyepichlorhydrine homopolymer [24], poly(phthalazinone ether ketone) [25] and poly(phthalazinone ether sulfone ketone) [26] were successfully synthesized by the above described

process. However, most of these polymers reported low IC values and were also unstable in high alkaline conditions as well as at elevated temperatures [27]. The loss in stability was due to the excessive water uptake at high temperatures. For moderate pH applications, the mechanical strength limitation of the AEMs was overcome by blending the base hydrophilic polymer containing the carrier group with a mechanically stable hydrophobic polymer [28-31].

Polysulfone (PSf) is widely chosen as the starting material for the synthesis of solid polymer AEM for low temperature applications due to its excellent stability and ease of its chemical structural modification [14-20]. However, the quaternary ammonium groups added to the PSf as hydroxide carrier groups resulted in low IC values especially at elevated temperatures [16, 19, 20]. Addition of quaternary phosphonium as ion carrier group to PSf resulted in a very stable and strong AEM with a high IC [32] for moderate temperatures. However this kind of membrane was having high solubility in alcohols, thus limiting its application in direct alcohol fuel cells (DAFC). Imidazolium was identified as an excellent choice for carrier group due to its excellent thermal stability, low volatility, selective solubility and wider electrochemical range [33]. Imidazolium functionalized polysulfone (PSf-ImOH) membrane was successfully synthesized and this membrane was able to achieve high IC, good stability and desired solubility [34 - 36]. However, PSf-ImOH membrane having a high ionic conductivity (IC) was highly unstable, even at room temperature. This was because of the excessive water uptake by the ion carrier groups. Hence, this kind of membranes was not used for AFC application studies.

Polyvinylidene fluoride (PVDF) is widely used as a hydrophobic and thermos-mechanically stable polymer. Radiation grafted PVDF has been successfully used for AEM development [37]. However, the degradation of the polymer in high alkaline media made it unfit as a starting material for AEM construction [38-40]. But, PVDF has been successfully used as blending agent with ion conducting polymers for moderate pH applications [41, 42]. The crystalline nature of PVDF imparts the desired hydrophobicity, insoluble nature in low boiling water soluble solvents and thermo mechanical stability to the base polymer group.

In this current study, a novel series of PVDF-PSf-ImOH blend membranes were synthesized by varying the weight ratio of these two polymers. The prepared AEMs were characterized with respect to structural morphology, water uptake, swelling ratio, membrane solubility, thermal stability, IEC and IC. Also, studies on the membranes AEM properties with respect to temperature changes were carried for understanding the behavior of the blend membranes at elevated temperatures (50-80°C). The best performing AEM was further compared against the pure PSf-ImOH (having the like IEC) and the results are discussed.

2. Experimental Procedure

2.1. Materials

Materials used for synthesis of the PVDF-PSf-ImOH blend anion exchange membranes are as specified: Udel P3500 polysulfone (PSf) was procured from Solvay plastics Ltd.; Polyvinylidene fluoride (PVDF) (Kynar 761A grade) was supplied by membranes research laboratory of National Institute of Technology (NIT) - Trichy, India; N,N-dimethylformamide was obtained from S D Fine-

Chem Limited of Mumbai, India. All other chemical reagents like trichloromethylsilane, chloroform, paraformaldehyde, stannic chloride, 1-methylimidazole, acetone, methanol, ethanol, diethyl ether, sodium hydroxide, hydrochloric acid, potassium hydroxide and phenolphthalein indicator were obtained commercially from TCI Chemicals, India and were used as such in the membrane preparation process without any further treatment. All the materials used for synthesizing the membranes were of analytic grade. Freshly prepared deionized water was used in the membrane preparation process.

2.2. Synthesis of PVDF - PSf-ImOH anion exchange membrane

PVDF-PSf-ImOH blend membrane was prepared by a 2- step process, i.e., preparation of imidazolium chloride-functionalized polysulfone (PSf-ImCl) followed by blending of PVDF with PSf-ImCl and subsequent alkalization.

2.2.1. Preparation of imidazolium chloride-functionalized polysulfone

Chloromethylated polysulfone (CMPSf) was prepared by the synthesis principle described by Avram et al. [43] using trichloromethylsilane as the chloromethylating agent. Particularly, 3 g of PSf was added to 150 mL of solvent chloroform in a round bottomed flask. After complete dissolution of PSf in chloroform, 17 mL of trichloromethylsilane was added drop wise to the flask. To this solution, 4.6 g of paraformaldehyde was added. The mixture was continuously stirred for an hour. During the course of stirring, 0.3 mL of Stannic chloride was added drop wise to accelerate the reaction. The flask was then maintained in a water bath of $50 \pm 0.1^{\circ}$C for four days. The chloromethylated polymer product was precipitated in ethanol. The precipitate was washed with ethanol and then with deionized water. The product was vacuum dried for 12 h at 50°C.

Following the preparation of CMPSf, PSf-ImCl was synthesized from CMPSf using 1-methylimidazole, based on Menshutkin reaction [44]. Specifically, 2 g of CMPSf was added to 20 mL of 1-methylimidiazole and was stirred till dissolution. The solution was then heated to 80°C for a period of 30 min. The solution was then poured into excess acetone to precipitate out PSf-ImCl. The product was then washed with acetone and deionized water. Subsequently the product was vacuum dried at 80°C for 24 h. The process chemistry for PSf-ImCl synthesis is shown in Fig. 1.

2.2.2. Blending of PVDF with PSf-ImCl followed by alkalization

Blend membranes made of PVDF and PSf-ImCl were prepared by mixing PVDF with the synthesized PSf-ImCl at different weight ratios as shown in Table 1. The total weight was fixed to 5 g. Specifically, both the PVDF and PSf-ImCl powders were mixed in a conical flask with 100 mL of N,N-dimethylformamide as solvent at the required ratios. After the complete dissolution of the polymeric mixture in the solvent, the solution was poured into a petri dish to cast the membrane and dried in a vacuum oven at 60 °C for 90 min. After complete evaporation of solvent, the blend PVDF-PSf-ImCl membranes were peeled off the petri dish. PVDF-PSf-ImOH membranes were finally obtained by alkalization of the prepared membranes using 1 M potassium hydroxide (KOH) at room temperature

for 24 h. The membranes were then washed in deionized water to remove any residual KOH and vacuum dried at 60°C for 24 h.
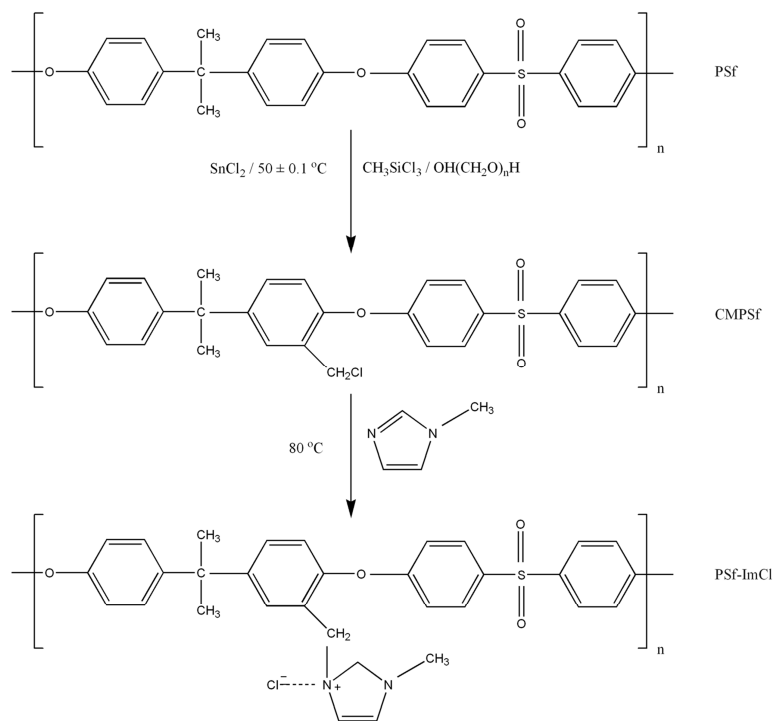

Fig. 1. Synthesis scheme of PSf-ImCl.

2.3. Structural characterization by ^{1}H NMR

Successful synthesis of CMPSf and the degree of chloromethylation in the CMPSf polymer was determined using ^{1}H NMR spectroscopy. The spectral analysis was conducted with Bruker NMR at a resonance frequency of 399.7 MHz. 5 mg of synthesized CMPSf was dissolved in 0.5 mL of deuterated chloroform and the resulting solution was subjected to the proton NMR (^{1}H NMR) analysis. Tetramethylsilane was used as the internal standard in all the cases for the interpretation of the results.

2.4. Ion exchanging capacity (IEC)

Determination of the IEC for the synthesized blend membrane was done by the back titration method. Particularly, 0.3 g of the blend membrane sample was kept immersed in 50 mL 0.01 M HCl standard solution for 24 h. The IEC of the membrane samples were then calculated by back titration with 0.01 M NaOH standard solution using phenolphthalein indicator. The 50 mL 0.01 M HCl

standard solution was used as the blank sample for IEC determination. Prior to the IEC determination, the membrane samples were vacuum dried for 10 h at 80°C to remove any moisture content present in the sample. The IEC for the prepared membranes was calculated using Eq. (1).

$$IEC = \frac{(V_b - V_s) \times C_{HCl}}{W_{dry}} \qquad (1)$$

where V_b is the volume of NaOH consumed for blank solution titration, V_s is the volume of NaOH consumed for membrane sample titration, C_{HCl} is the concentration of HCl solution and W_{dry} is the weight of the dry membrane.

2.5. Water uptake and swelling ratio

Rectangular cuts of the blend membranes were prepared and placed in separate deionized water baths at room temperature for 24 h. The membranes were then surface cleaned using dry filter paper and the wet weight and wet dimensions of the membranes were measured. Subsequently, the wet membrane samples were vacuum dried at 80°C for 12 h and the dry weight and dry dimensions of the membranes were measured. The water uptake and swelling ratio (area basis) of the membranes were calculated using Eqs. (2) and (3).

$$Water\ Uptake\ (WU) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (2)$$

$$Swelling\ Ratio\ (SR) = \frac{D_{wet} - D_{dry}}{D_{dry}} \times 100 \qquad (3)$$

where W_{wet} and W_{dry} are the weights of the wet and the dry membrane sample, respectively; D_{wet} and D_{dry} are the average dimensions [$D_{wet} = (D_{wet1} \times D_{wet2})^{1/2}$, $D_{dry} = (D_{dry1} \times D_{dry2})^{1/2}$] [45] of the wet and the dry membrane sample, respectively. D_{wet1} and D_{wet2} are the length and width of the wet membrane sample and D_{dry1} and D_{dry2} are the length and width of the dry membrane sample, respectively. Temperature variation studies (from 20 to 80°C) of water uptake and swelling ratio for the prepared blend membranes were also carried out.

2.6. Membrane solubility

Solubility of the synthesized PVDF-PSf-ImOH blend membrane was qualitatively tested in four low boiling point water soluble solvents such as acetone, diethyl ether, methanol and ethanol. About 100 mg of the blend membrane samples were taken and vacuum dried at 80°C for 12 h to remove any moisture content in the samples. The membrane samples were then added to 50 mL of the said solvents at room temperature and the solubility of the membrane samples in each of the solvent was measured after 36 h.

2.7. Thermal stability

Thermal stability analysis of the synthesized PVDF-PSf-ImOH blend membrane was carried out using thermogravimetric analyser STA 409PC Seiko Instruments Inc. A sample of 100 mg of the prepared membrane was heated from 100°C to

750°C with a constant heating rate of 10°C min^{-1} under air atmosphere conditions. Prior to the thermal stability study, the membrane samples were vacuum dried for 10 h at 80°C to remove any moisture present in the membrane sample. Glass transition temperature (T_g) of the respective membrane samples were also determined by differential scanning calorimetry TA Instruments 2920 DSC.

2.8. Ionic conductivity (IC)

Ionic conductivity (IC) of the synthesized PVDF - PSf-ImOH blend membrane was measured using the normal four-point AC impedance method. The Tech-science services A18001 equipment was used as the impedance analyzer over a frequency range of 1 to 10^6 Hz. Prior to IC determination, the membrane samples were placed in deionized water for 24 h for complete hydration. To ensure the 100% relative humidity during IC measurement, the probe and the membrane were completely immersed in the deionized water at room temperature. Based on the resistance derived from the impedance plot, ionic conductivity of the membrane samples is calculated using Eq. (4).

$$IC = \frac{L}{(Wd) \times R} \tag{4}$$

where L is the distance between the two potential electrodes, d and W are the thickness and width of the membrane sample, respectively and R is the resistance value derived from the complex plane impedance plot. IC variations of the prepared blend membranes with respect to change in temperature (from 20°C to 70°C) were also studied.

3. Results and Discussion

3.1. ^{1}H NMR

^{1}H NMR spectra of the prepared CMPSf is shown in Fig. 2. Characteristic phenylic hydrogen observed between 6.7 and 7.8 ppm shifts confirmed that the polymer backbone was polysulfone. The shift at 1.7 ppm corresponded to the methylic hydrogen in polysulfone. On the other hand, characteristic peak at 4.54 ppm confirmed the attachment of chloromethyl moiety. The degree of chloromethylation (DC) was calculated by integrating the peaks under 4.54 and 7.8 ppm shift and it was reported to be 180%.

$$Degree\ of\ Chloromethylation\ (DC\ in\ \%) = 2 \times \frac{A_{4.54}}{A_{7.8}} \times 100 = 2 \times \frac{1}{1.11} \times 100 = 180\%$$

3.2. Ion exchange capacity

IEC measurement for a given AEM is a characteristic feature indicating the AEM's performance and could be used as a qualitative measure for the water uptake, swelling ratio and ionic conductivity of the membrane [4]. The measured IEC values for the synthesized membranes are shown in Table 1. The IEC values of the blended membranes recorded an increasing pattern with the increasing concentration of PSf-ImOH in the blend, clearly indicating that the predominant carrier group for the blend membrane is PSf-ImOH. The IEC values obtained for the blend membranes were better, in comparison to that of PSf-quaternary

ammonium hydroxide membranes (0.92 mmol g^{-1}) [46] and PSf-quaternary phosphonium hydroxide membranes (1.23 mmol g^{-1}) [32]. The higher IEC values for the PSf-ImOH membranes are due to the excellent ion-exchanging functionality of the imidazolium functional group [33] and also due to the complete conversion of the chloromethylated group to the imidazolium group by the Menshutkin reaction [44].
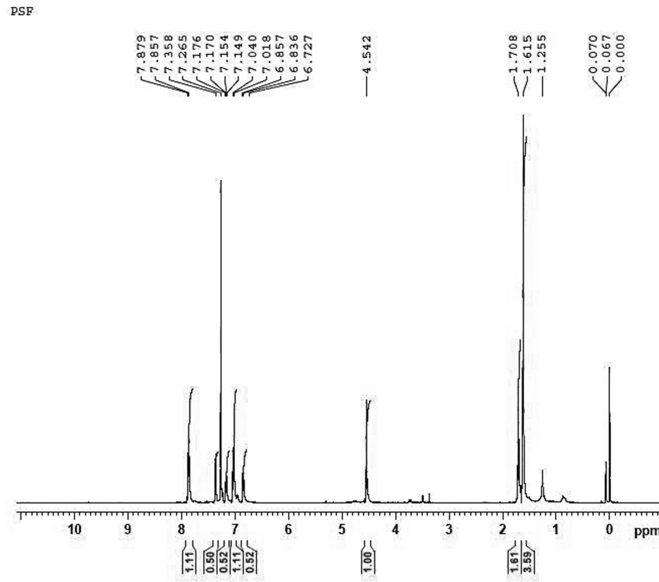

Fig. 2. ^{1}H NMR analysis of CMPSf.

Table 1. IEC values of the PVDF-PSf-ImOH blend membranes.

Membrane blend composition (in weight %)		IEC (mmol g^{-1})
PVDF	**PSf-ImOH**	
30	70	2.62
50	50	2.38
70	30	2.11

3.3. Water uptake and swelling ratio

Water uptake and swelling ratio analysis for an AEM gives a qualitative indication of the integrated morphology, mechanical properties and ionic conductivity of the membrane thus judging the potential use of the membrane for commercial fuel cell application [4]. Figure 3 presents the result of the water uptake of the prepared membranes at 20°C. Studies showed that the 30% PVDF blend membrane had an unexpected low water uptake value of 10 % only, although it possessed a high IEC. This might be due to the dissolution of the ion conducting ImOH group in water, leaving behind the hydrophobic PVDF polymer part in the membrane. The dissolution of ImOH group could be explained by the relative instability PSf-ImOH with PVDF. However, with increase in the PVDF

concentration in the blend membrane, the stability of blend membrane increased and a water uptake value of 64% was recorded by the 50% PVDF blend membrane. The decreased water uptake value of 23 % by the 70% PVDF blend membrane could be attributed to the increased concentration of the hydrophobic PVDF part in the blend membrane.

Figure 4 shows the result of the water uptake of the prepared blend membranes at temperature ranging from 20°C to 80°C. Water uptake of the blend membranes increased slowly at lower temperatures and faster at higher temperatures. The 70% PVDF recorded a water uptake from 23% to 72% with a temperature rise from 20 to 80°C and was having a stable structure and much integrated morphology with the temperature changes. The water uptake of the 30% PVDF blend membrane was quite less (< 20%) due to the dissolution of the carrier polymer, PSf-ImOH, in the water and thereby indicating the less ionic conductivity nature of the membrane when applied to fuel cells. The 50% PVDF blend membrane recorded a maximum water uptake of 290% at 70°C and further raise in temperature resulted in gel formation of the blend membrane because of the excessive hydrophilicity of the membrane as indicated by the IEC value of the membrane.
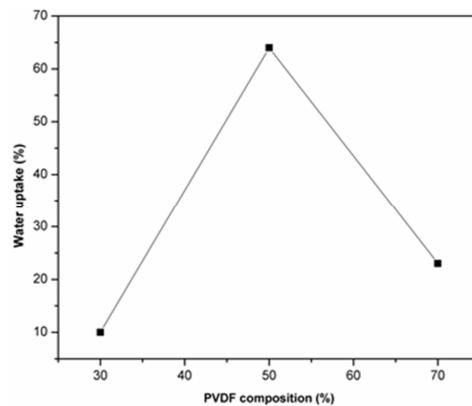

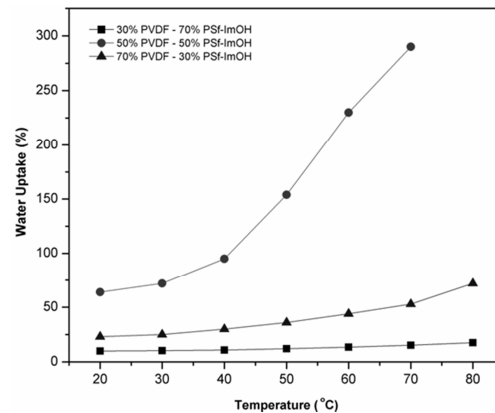**Fig. 3. Water uptake of PVDF-PSf-ImOH blend membranes at 20°C.**

Fig. 4. Water uptake of PVDF-PSf-ImOH blend membranes at different temperatures.

Result of the swelling ratio analysis with respect to temperature variation is shown in Fig. 5. Swelling ratio of 30% PVDF blend membrane was comparatively constant with temperature, clearly resembling the nature of pure PVDF, as the carrier polymer group got dissolved in water during the test. The 70% PVDF blend membrane recorded a better swelling ratio value in comparison with the other prepared membranes.

Analysis of the results of both the tests, it was clear that the 70% PVDF membrane possessed the required water uptake and swelling ratio values which corresponds for a better performing AEM [4]. Hence the 70% PVDF membrane has a promising application for fuel cell studies.
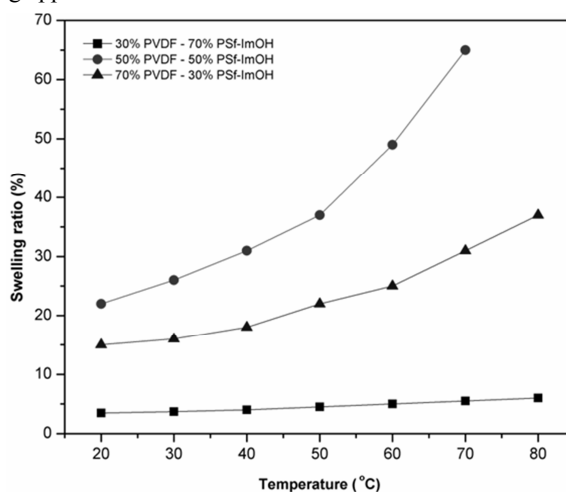

Fig. 5. Swelling ratio of PVDF-PSf-ImOH blend membranes at different temperatures.
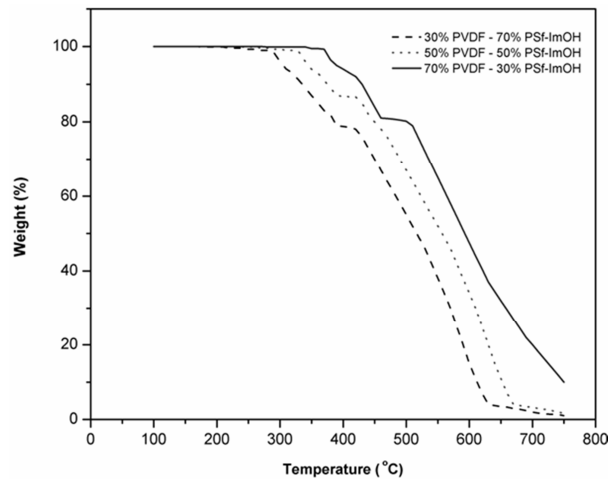
3.4. Membrane Solubility and Thermal stability

Solubility results of the prepared blend membranes in solvents like methanol, ethanol, diethyl ether and acetone are shown in Table 2. All the blend membranes were insoluble in methanol and ethanol thus showing excellent alcohol tolerance. The 30% PVDF and 50% PVDF blend membranes showed a slight solubility (2 and 3.5% weight loss respectively) in diethyl ether solvent while 70% PVDF blend membrane was completely insoluble owing to the crystalline nature of PVDF. All blend membranes were insoluble in the acetone solvent.

TGA curves for the prepared blend membranes are shown in Fig. 6. All the blend membranes exhibited a similar pattern of three weight loss steps. The first weight loss step is due to removal of the imidazolium group from the conducting polymer chain by nucleophilic substitution. The second weight loss step is due to the removal of the residual hydroxylmethylene and methyl groups as well as the main polysulfone chain decomposition and the third weight loss step is ascribed to the decomposition of the PVDF polymer chain.

**Table 2. Solubility of PVDF - PSf-ImOH blend
membranes in low boiling water soluble solvents.**

Membrane blend composition (in weight %)		Solubility in			
PVDF	PSf-ImOH	Methanol	Ethanol	Diethyl ether	Acetone
30	70	Insoluble	Insoluble	Slightly Soluble	Insoluble
50	50	Insoluble	Insoluble	Slightly Soluble	Insoluble
70	30	Insoluble	Insoluble	Insoluble	Insoluble

Fig. 6. TGA curves of PVDF-PSf-ImOH blend membranes.

Results of the thermal stability studies showed the increased thermal stability of the blend membranes with the increasing concentration of PVDF in them. The primary decomposition observed in all the blends confirms the characteristic presence of imidazolium functional carrier group [36]. Glass transition temperatures of the blend membranes, as shown in Table 3, indicated the enhanced thermal stability of the blend membranes when compared with the polysulfone - quaternary ammonium hydroxide membranes ($T_G = 120^oC$) [46], polysulfone - quaternary phosphonium hydroxide membranes ($T_G = 185^oC$) [32] and pure PSf-ImOH ($T_G = 258^oC$ for 120% DC) [36].

Table 3. Glass Transition values of the PVDF-PSf-ImOH blend membranes.

Membrane blend composition (in weight %)		Glass Transition Temperature (in ^oC)
PVDF	PSf-ImOH	
30	70	295
50	50	336
70	30	380

3.5. Ionic conductivity

IC values of the prepared blend membranes at 20°C are shown in Table 4. IC of 70% PVDF blend membrane recorded a value of 51 mS cm^{-1}. The 50% PVDF blend membrane showed, only a slightly higher IC value (54 mS cm^{-1}) than that of the 70% PVDF. The IC value of 50% PVDF was not as expected leading to a conclusion of partial dissolution of the carrier group in water which may be due to lack of strong stability in blending. The 30% PVDF blend membrane recorded a low IC value of 4.7 mS cm^{-1} as expected from the results of water uptake and swelling ratio test. The IC value for the 70% PVDF blend membrane was higher than that of polysulfone - quaternary ammonium hydroxide membranes (~19 mS cm^{-1}) [46] and polysulfone - quaternary phosphonium hydroxide membranes (45 mS cm^{-1}) [32]. The value was also comparable with that of pure PSf-ImOH (53 mS cm^{-1}) of 132% DC which was having an excessive water uptake of 170% at 20°C [36].

Figure 7 shows the IC variation of the blend membranes with change in temperature from 20°C to 70°C. As expected, the IC values of the membranes increased with the increasing temperature due to enhanced convection currents of water through the carrier group in addition to Grotthuss mechanism [4]. The IC value of the 70% PVDF blend membrane exhibited an appreciable increase in value from 51 mS/cm (at 20°C) to 82 mS/cm (at 70°C) matching with the IC value of the 50% PVDF at 70°C. The 30% PVDF blend membrane maintained almost a constant low IC value, thus exhibiting the inert nature of PVDF with respect to change in temperature.

Table 4. IC values of the PVDF - PSf-ImOH blend membranes.

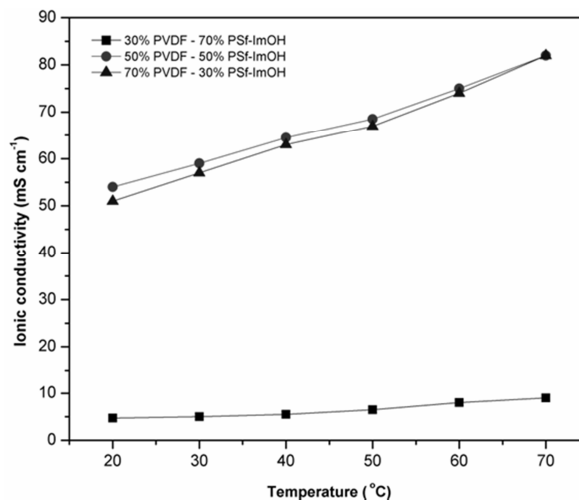| Membrane blend composition (in weight %)		IC (mS cm^{-1}) at 20°C
PVDF	PSf-ImOH	
30	70	4.7
50	50	54
70	30	51

**Fig. 7. Ionic Conductivity of PVDF-PSf-ImOH blend membranes.**

3.6. Comparison with pure PSf-ImOH membrane

Analyzing the AEM characterization of the synthesized blend membranes, it was very clear that the 70% PVDF blend membrane possessed the better features for the application in fuel cells. The water uptake and swelling ratio values for the membrane were nominal. The enhanced thermal stability of the 70% PVDF membrane makes it a better candidate for high temperature fuel cells like DAFC. The IC value of the membrane was also quite high in comparison to other AEMs synthesized so far. The features of the 70% PVDF blend membrane was compared against the pure PSf-ImOH membrane.

Comparison of the water uptake and hydroxide conductivity of the 70% PVDF blend membrane with that of pure PSf-ImOH membrane (DC of 124%), having the same IEC (=2.1 mmol g^{-1}) as that of the blend membrane, is presented in Figs. 8(a) and 8b respectively. The comparative study was mainly carried out to study the stability nature and better performance of the blend membrane than the pure PSf-ImOH membrane for the same IEC value. The pure PSf-ImOH membrane was freshly synthesized for the comparative study and the value of its IEC agrees with the work of Yan et al. [36]. Figure 8(a) clearly shows that the blend membrane was having a water uptake, 5 times less at low temperatures (20-40°C) and 8.5 times less at high temperatures (60°C), than that of the pure PSf-ImOH membrane. With respect to temperature changes, the better hydroxide conductivity of the blend membrane than the pure PSf-ImOH membrane is clearly illustrated in Fig. 8(b). The PVDF portion of the blend membrane has regulated the water uptake of the blend membrane thereby resulting in a stable morphology and better conductivity than the pure PSf-ImOH membrane.
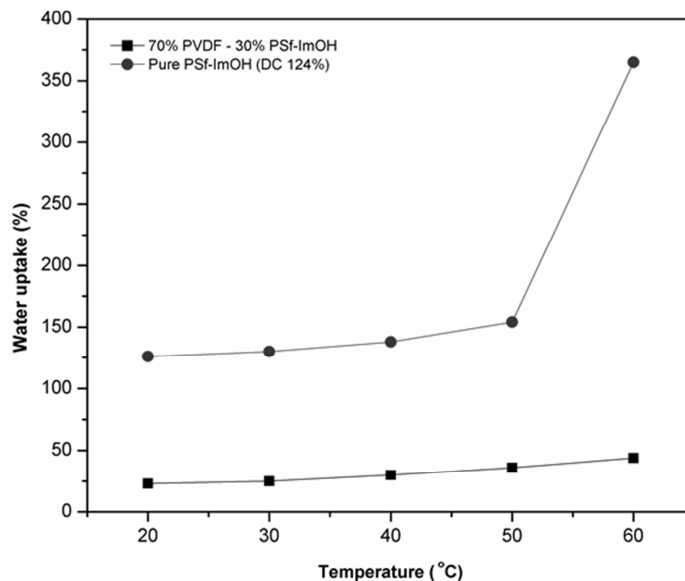
(a). Water uptake.
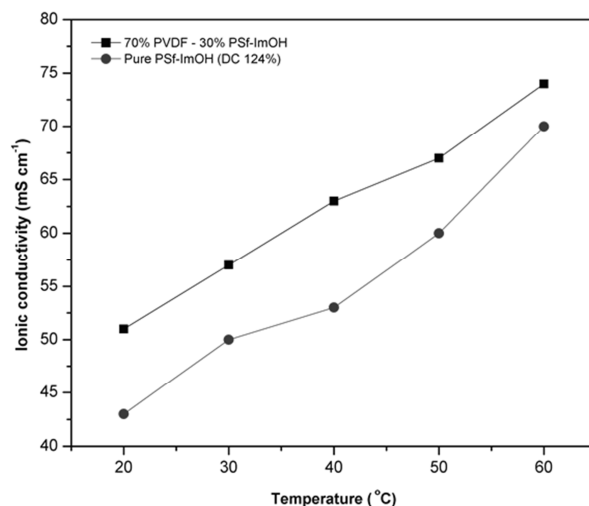
(b). Ionic conductivity.

**Fig. 8. Comparison between 70% PVDF
blend and Pure PSf-ImOH at different temperatures.**

4. Conclusions

Although imidazolium functionalized polysulfone (PSf-ImOH) membrane is one of the promising anion exchange membrane (AEM) for low temperature fuel cell applications. However, at high levels of ion exchange capacity (IEC), the membrane's water uptake and swelling ratio increases rapidly especially with temperature rise thus destabilizing it and making it unfit for high temperature alkaline fuel cells. To overcome this limitation, PSf-ImOH with a high degree of chlorination (DC) was blended with polyvinylidene fluoride (PVDF), which is thermally stable and highly hydrophobic polymer. A novel series of PVDF-PSf-ImOH blend membrane was prepared in different weight ratios (PVDF/PSf-ImOH: 30/70, 50/50 and 70/30) and was subjected to AEM characterization. ^{1}H NMR analysis confirmed the high degree of chlorination (180%) in the prepared Chloromethylated polysulfone (CMPSf) which was completely converted to imidazolium chloride through Menshutkin reaction and subsequently to imidazolium hydroxide by alkalization. IEC studies revealed that the predominant ion carrier group for the blend membranes is PSf-ImOH and the IEC values of the blend membranes showed an increasing pattern with increasing concentration of PSf-ImOH in the blend. Water uptake and swelling ratio analysis indicated the better performance of the 70% PVDF blend membrane, especially in terms of integrated morphology of the membrane at high temperatures. This was due to high blending strength of the polymers in the membrane. Solubility and thermal stability tests indicated the increased stable nature of the 70% PVDF blend membrane assuring the application of the membrane to high temperature DAFC. Ionic conductivity (IC) studies on the blend membranes clearly showed that the 70% PVDF blend membrane was having a better IC value at low temperatures and high IC value at high temperatures compared to other blend membranes.

Comparative studies of the 70% PVDF blend membrane with pure PSf-ImOH (DC of 124%) clearly revealed the less water uptake and high hydroxide conductivity of the blend membrane than the pure PSf-ImOH. In summary, the 70% PVDF blend membrane gave promising AEM characterization features suggesting to its potential application in fuel cell applications especially for high temperature working condition.

Acknowledgement

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