

Functionalized Polysulfones as an Alternative Material to Improve Proton Conductivity at Low Relative Humidity Fuel Cell Applications

Khalfan Abdulla Said,¹ Ibrahim Saana Amiinu,¹ Haining Zhang^{* 1,2} and Mu Pan^{1,2}.

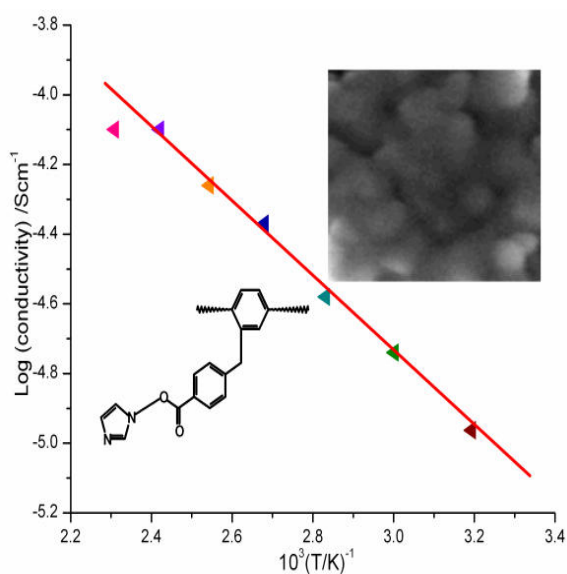
1. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, P.R. China, 430070.

2. Hubei Key Laboratory of Fuel Cells, Wuhan University of Technology, Wuhan, P. R. China, 430070.

*E - mail of corresponding author: haining.zhang@whut.edu.cn Tel.:+86 139 7164 3961. Fax: +86 27 87879468.

ABSTRACT

Polysulfones (udel) was chemically functionalized by bonded functional groups to the main chain through chemical reaction and investigated for use as proton-conducting fuel-cell membranes. The resulting ionomers were cast into membranes and properties such as thermal stability, ion-exchange capacity, proton conductivity and water sorption were evaluated. The modified polymers were characterized by nuclear magnetic resonance (NMR) and infrared spectroscopy (FT-IR). Thermo gravimetric analysis (TGA) show that these membranes are thermally stable up to 480°C in dry air, which implying that they have a good potential to be used as the membranes for high-temperature PEM fuel cells. Under anhydrous circumstances, ionic conductivity of the membrane hit the highest point value of 7.94×10^{-5} at 160 °C related with the activation energy of 11.6 kJ mol^{-1} for proton transport. The surface morphology of the formed membrane was examined using atomic force microscopy and scanning electron microscopy.



Keywords: Proton conducting materials, relative humidity, Polysulfone, Chloromethyl benzoic acid, imidazol-1-yl 4-methylbenzoate,

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are the latest promising energy producers designed for the future century. At the present capable of providing power for a variety of wide applications from portable electronics, automotive transportation and military devices. Proton exchange membrane fuel cells in general have a high power density, its ability to provide an ionic path for protons to travel from the anode to the cathode, moderately efficient in their conversion of chemical energy to electrical energy, low operating temperatures and low greenhouse gas emissions. ^[1-4]

Electrolyte is one of the main parts of fuel cell; in proton exchange membrane fuel cell electrolyte is in the form of plastic which made from polymery molecule and known as membrane. The majority of common polymer electrolyte membranes used in fuel cells applications are perfluorinated polymer membranes, e.g. DuPont's Nafion membranes. These membranes consist of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendant side chains. The structures of Nafion make a micro phase-separated morphology of membranes and thus they exhibit excellent thermal, mechanical, and electrochemical properties. ^[5]

Although the problems of Nafion are high cost, high methanol crossover through membranes and low proton conductivity at high temperature (low humidity circumstances) so Nafion is unstable at high temperature because conduct proton only in presence of water which limits the fuel cell operating temperature to be less than 80°C. ^[6]

The development of innovative membrane for use in fuel cells which can function at a temperature range $>100^{\circ}\text{C}$ is a highly attractive objective for researchers.^[7]

In recently there have been extensive research efforts how to find another fuel cell membrane that are stable at high temperature, low cost, and possess similar performance as the standard Nafion membrane.^[8, 9] For several years a number of Polymers have been investigated intensively for their possible as membrane materials in polymer electrolyte membrane fuel cell. Research groups have bought to improve the existing materials and to find substitute polymer that posse's similar performance as the standard Nafion membrane.^[11]

Aromatic polymers like polysulfones are future replacement of perfluorinated materials; these materials met most of the specifications of the fuel cell membranes, specifically high protonic conductivity, stability in oxidant and reducing, excellent mechanical, thermal, and chemical stability.^[10-11]

The low cost and easiness of processing have allowable many research groups all over the world to focus on their properties and characteristics. Most of available polysulfones, udel has been mostly reported in the literature. The reason is that; this polymer is soluble in a group of organic solvents compared to other polysulfones like radel, which enables to use different reactions for the chemical modification such as Electrophilic substitution and nucleophilic reaction.^[11] Chemical modification of the polysulfones by introducing new reactive functional groups to the main chain proved to be a useful way to change their properties, such as thermal behaviour, conductivity, flexibility and mobility and increase the reactivity of the main chain that permit further chemical reactions.^[11-16]

A number of reviews have been reported on the chemical modification of polysulfone by different mechanisms for the introduction of functional groups onto the polysulfone backbone. The modification of polysulfone is mostly based on adding various functional groups, such as carboxylic, fluorine, and methyl chloride to the aromatic ring, and by through sulfonation, nitration, and lithiation.^[17, 18]

To achieve the research objective, we are focusing on developing new proton electrolyte membrane to replace water. Some heterocyclic compounds, such as imidazole^[19] have been reported having high proton conducting ability. Imidazole has conventional many credits as it undergoes a very similar behaviour toward proton to that of water, as well as amphoteric molecules, hydrogen-bonded changeable networks, and self-dissociation. Compared with perfluorosulfonic polymer membranes in which the proton conductivity depends seriously on humidity, PEMs based imidazole^[20] may allow fuel cell operation above 100°C without the need of humidification, which could minimize or eliminate some of the key difficulties facing PEM fuel cells, including CO poisoning and the management of water, heat, and pressure. In this work, we focusing the development of polymer membranes capable at low humidity PEMFCs application based on polysulfones - imidazol-1-yl 4-methylbenzoate functionalize.

Recently the use of imidazole and its derivatives have been considered by many researchers.^[23-25] Membranes obtained by attaching the imidazole unit to short and stiff aromatic side chains controlled water uptake to the membrane. By placing the cohesion of the hydrophobic main-chain polymer phase was retained despite the formation of a highly water-swollen phase. Placing the imidazole units on side chains proved particularly beneficial to retain reasonable water uptakes at high IECs. Subbaraman, et al^[21] and Kim et al^[22] shows that replacement of water by N-heterocycles in Nafion membrane can significantly improve the proton conductivity of these membranes under anhydrous conditions..Imidazole also acts as a proton donating groups through the dissociation of the proton from the -NH group in imidazole. The conductivity of liquid imidazole was reported as high as 10^{-3} S/cm at the melting point of 90°C .^[20] The imidazole grafted polymer shows noticeable proton conductivity at high temperature without external humidification.

2. EXPERIMENTAL SECTIONS

2.1 Materials

Polysulfone (Udel) polymers were purchased from Solvay Advanced Polymers and dried at 100°C under vacuum before use. Chloromethyl benzoic acid and imidazole was purchased from Sinopharm Chemical Reagent Co. Ltd., China and used as received. Stannic tetrachloride (SnCl_4) as a catalyst, N, N-dimethyl acetamide (DMAc) Hydrochloric acid, and methanol were purchased from commercial source and used in the synthesis. Each reagent were purchased from commercial vendors and used without further purification unless specified.

2.2 The modification of polysulfones (PSF)

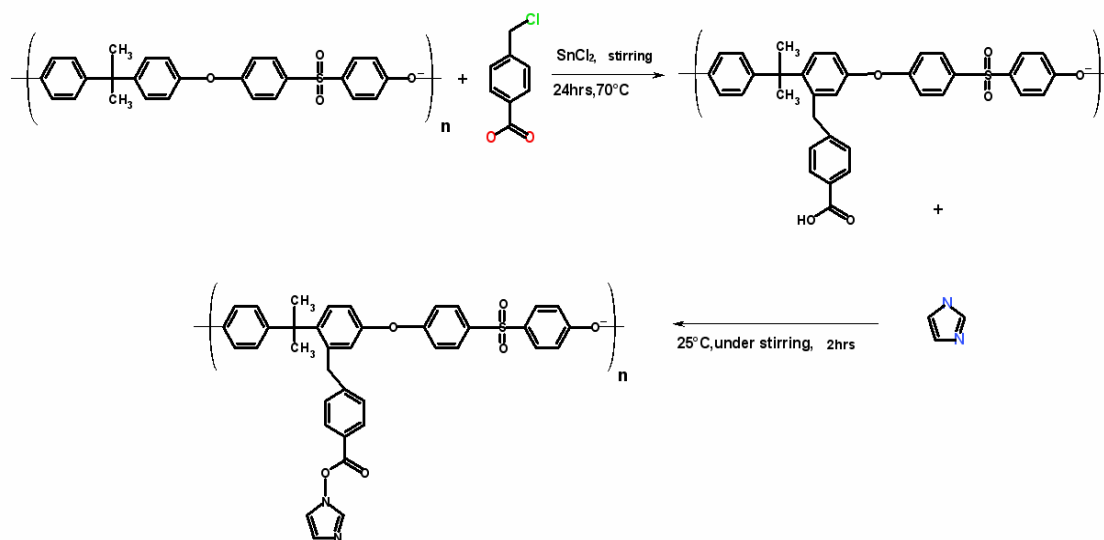
The modification of PSF was carried out according to Scheme 1. In the first step, PSF was functionalized with methyl benzoic acid side chains through the following procedures. In the 250 mL three neck bottled flask which completely dried, equipped with a magnetic stirrer and condenser, 80 ml of dimethyl acetamide (DMAC) was

added and 2g of polysulfones (PSF). Make sure all PSF is totally dissolved then add 10g of chloromethyl benzoic acid (CMBA) and 0.18g of Tin (IV) chloride, Keep it in 70 °C with reflux condenser and stirring for 24h, to maintain Friedal-Crafts between CMBA and PSF.

The resulting solution was poured into ethanol under stirring to get the precipitation. The polymer precipitate was filtered and rinses with Dilute Hydrochloric Acid to remove Tin (IV) chloride. After that wash with ethanol and DI water and finally dry in vacuum oven to constant weight of PSFMBA.

2.3 Membrane preparation

One gram of PSFMBA copolymer was dissolved in N, N-dimethyl acetamide (DMAc) as solvent to prepare a 10% (w/v) solution of PSFMBA. Then 2 gram of Imidazole was then added in slight excess, and the mixture was stirred at room temperature for 2 hrs. The resulting solution was cast on a pre-cleaned glass substrate and heated in the open air at 80 °C for 24 h and 100 °C for another 24 h to remove the solvent. The freshly prepared membranes were immer- sed in water for at least 20 h to get rid of any solvent residues and other impurities, and were then dried in vacuum at 50 °C for 24 h. The membrane was ion-exchanged in a 0.5M HCl solution for at least 24 h, and then washed repeatedly in distilled water until constant pH was reached. The thickness of the prepared membranes was between 100 and 130 μm.



scheme 1. Chemical modification of polysulfones

2.4 Membrane characterization

The structural characterization ¹H NMR and ¹³C NMR was performed using BRUKER DRX400MHz spectrometer with deuterated dimethylsulfoxide (DMSO-d₆) as the solvent of all modified polysulfones and deuterated chloroform for the unmodified polysulfones.

Fourier transform infrared spectroscopy (FTIR) study of the membranes was performed using (FT-IR, Bio-Rad FTS 300) with a resolution of 4cm⁻¹ from 400 cm⁻¹ to 4000 cm⁻¹ as a means of investigating the chemical behavior of the various structures.

The water uptake was calculated by weighing the membrane under both hydrated and dry situations. First the membrane is immersed in water for 24 h, and then rapidly drying the surfaces with tissue paper and weighing to get the mass of the wet membrane (W_{wet}). After that, the membranes were dried in vacuum at 50 °C for 15h before determining the mass of the dry membrane (W_{dry}). The water uptake was then calculated as:

$$\text{Water uptake(\%)} = \frac{W(\text{wet}) - W(\text{dry})}{W(\text{dry})} \times 100$$

The proton conductivity of membranes can be measured by AC impedance spectroscopy. Two platinum electrodes were placed on the same face of membranes that were sandwiched between two PTFE sheets.

Conversely, it is generally easier to determine membrane conductivities by measuring the resistance in the plane of the membrane. This method allows for higher and more easily measurable resistances and a simplified set-up. The distance between the two electrodes was 1.5 cm. Impedance data were collected in the frequency range 10^{-1} – 10^7 Hz at amplitude of 100 mV. The membrane conductivity (σ , $S\text{ cm}^{-1}$) is calculated from the impedance data by using the following equation.

$$\sigma = \frac{s}{R \times t \times w}$$

Where s is the distance between two electrodes (cm), t is the thickness of membrane (cm), w is the width of the membrane and R is the membrane resistance obtained from the AC impedance data.

Thermo gravimetric Analysis (TGA) was performed using Elemental Analysis system (GmbHVarioEL) and NETZSCH STA 449 F3 Jupiter® thermal analyzer, respectively. The TGA heating rate was 10°C per min. over a temperature range of $50\text{--}900^\circ\text{C}$ under nitrogen atmosphere.

The surface morphology of the formed membrane was examined using atomic force microscopy (AFM, Nanoscope IV) under tapping mode. To determine the distribution of Imidazole inside the membrane, scanning electron microscopy (SEM, JEOL JSM-5610LV equipped with Energy Dispersive Spectrum Analyzer) of the cross-sectional direction of the membrane was performed. The sample for cross-sectional SEM images was obtained by fracturing it in liquid nitrogen

4. RESULTS AND DISCUSSION

Thermal stability of the membranes is a significant property that indicates the durability under fuel cell operation. The analysis was investigated by thermo gravimetric analysis (TGA) by heating the membranes at heating rate of $10^\circ\text{C}/\text{min}$ under N_2 and the results are shown in Figure 1. The membrane showed a total weight loss of $\sim 10.01\%$, over the temperature range of $150\text{--}235^\circ\text{C}$. This weight loss is due to removal of the residual water that is bound with the hydrophilic imidazole moieties, attributed to thermal desorption of physisorbed water and traces of residual organic solvents, respectively, from the hydrophilic character of the membrane and the solvents used in the synthesis. Beyond this temperature, the large weight loss occurred around $480\text{--}560^\circ\text{C}$ where by the material experiences a rapid weight loss due to thermal decomposition of imidazole group. The membrane shows a total weight loss about 57% at this stage

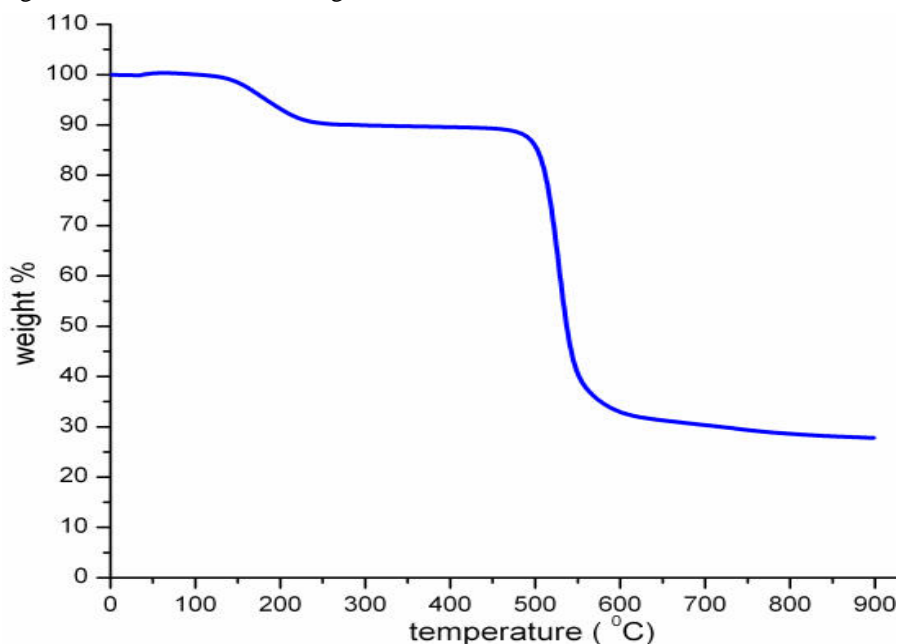


Figure 1 Thermo-gravimetric analysis curve of imidazole-1-yl 4-methylbenzoate-psf

The material further degrades gradually over the temperature range above 600°C , 2.21% weight loss corresponds to the main polymer chain decomposition. This temperature is higher than that of benzoyl

(difluoromethylene-phosphonic acid) PSF^[17] and Imidazolium functionalized polysulfone. From these results, it is concluded that, the membranes are thermally stable within the temperature range for PEMFC applications. The water uptake of PEMs has a considerable effect on membrane conductivity and mechanical properties;^[26-27] a high degree of water absorption is needed in order to ensure high proton conductivity. The behavior of proton-conducting ionomers containing water provides much information on how the material will behave under fuel cell conditions. Membranes with small water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with too high water sorption and if the water absorption is too high, the dimensional stability will suffer and the membrane may disintegrate due to the swelling pressure. The result of swelling shows that water sorption is increased with the increase of the concentration of imidazole group content, which is contributed by the strong hydrophilicity of the imidazole group in the polymer backbone. The Water uptake experiment shows that the amount of water absorbed by the membrane at 40°C is 43 %.

FTIR spectroscopy was used to characterize the polymers synthesized. The FTIR spectra of the unmodified and modified polymer are shown in Figure 1. Typical FTIR spectra of methyl benzoic acid-psf and imidazole-1-yl 4-methylbenzoate are shown in Figure 2(b) and (c) respectively.

Characteristic bands at 1705 cm⁻¹ in Figure 2 (b) and (c) were assigned to C=O stretching from benzoic acid. These observations indicated the successful grafting of methyl benzoic acid units onto PSF. These peaks are missing in figure 2(a).

Characteristic bands at 942 cm⁻¹, 1063 cm⁻¹ and at 1635 cm⁻¹ in Figure 2 (c) were assigned to (N-O), (N-C) and (C=N) stretching, respectively. These observations indicated the successful grafting of imidazole onto methyl benzoic acid-PSF. Compared with the unmodified polysulfones, these additional peaks are absent.^[28]

The ¹H NMR spectra of PSF, MBA-PSF and PSF- imidazol-1-yl 4-methylbenzoate are shown in Figure 3(a), 3(b), and 3(c) respectively, confirmed the successful introduction of the benzoic acid and imidazole side chains onto polysulfones.

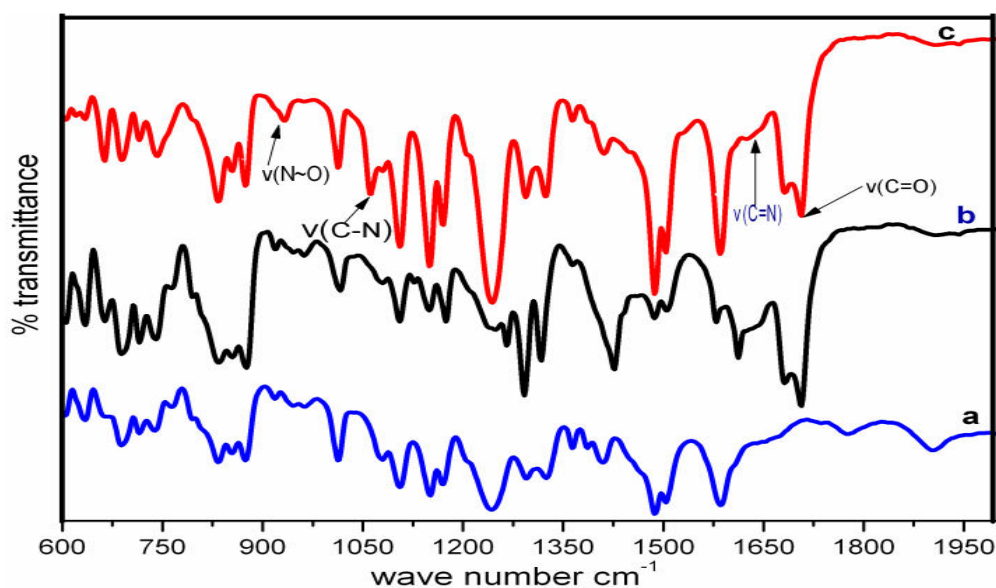


Figure 2 FT-IR spectra of psf (a), mba-psf (b) and imidazol-1-yl 4-methylbenzoate-psf

¹H NMR signals arising from the methyl protons at $\delta=1.6$ ppm and from the aromatic protons at $\delta=7.24-7.8$ ppm for all modified and unmodified polysulfones. Several new peaks are present in the spectrum of mba-psf, figure 3(b) at $\delta=8.4-8.64$ ppm, the peaks corresponding to Hydrogen atoms on the benzoic acid. In addition, new signals arose at $\delta=7.9-8.1$ ppm in (spectrum c) figure 4, which are ascribed to the protons of the imidazole.

The ¹³C NMR spectra of PSF, MBA-PSF and PSF- imidazol-1-yl 4-methylbenzoate are shown in Figure 4a, b and c respectively. The presence of the benzoic acid group is recognized by the new peaks at $\delta=127.6, 129, 133,$ and 172 ppm respectively in figure 4b. Shifts arising from the carbon atom carrying the nitrogen were found at $\delta=139$ ppm, 139.8 and 118.3 ppm in figure 4c. Both ¹H and ¹³C NMR spectra showed that the psf had been functionalized with imidazol-1-yl 4-methylbenzoate as preferred.

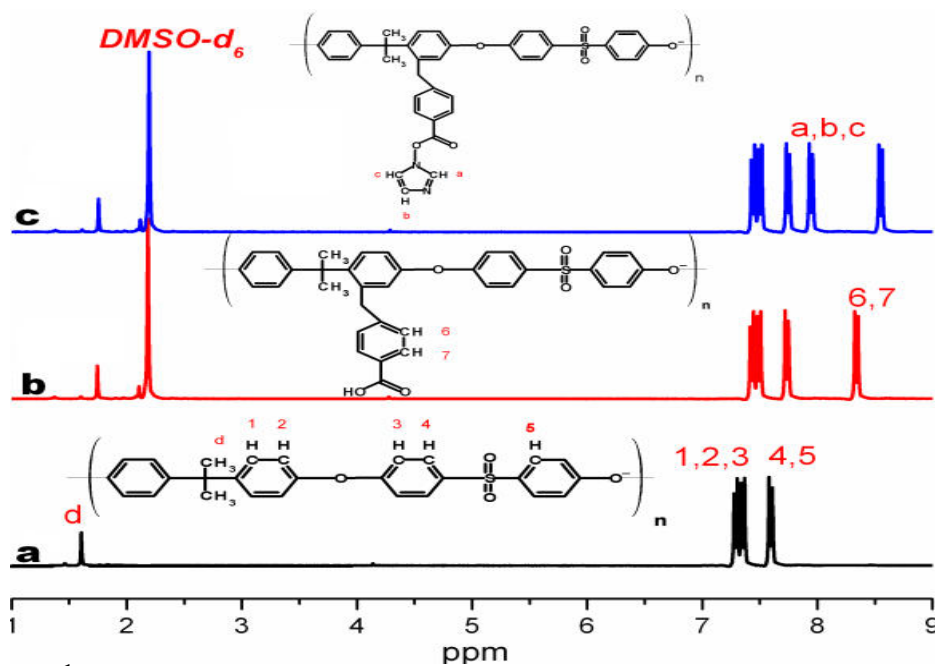
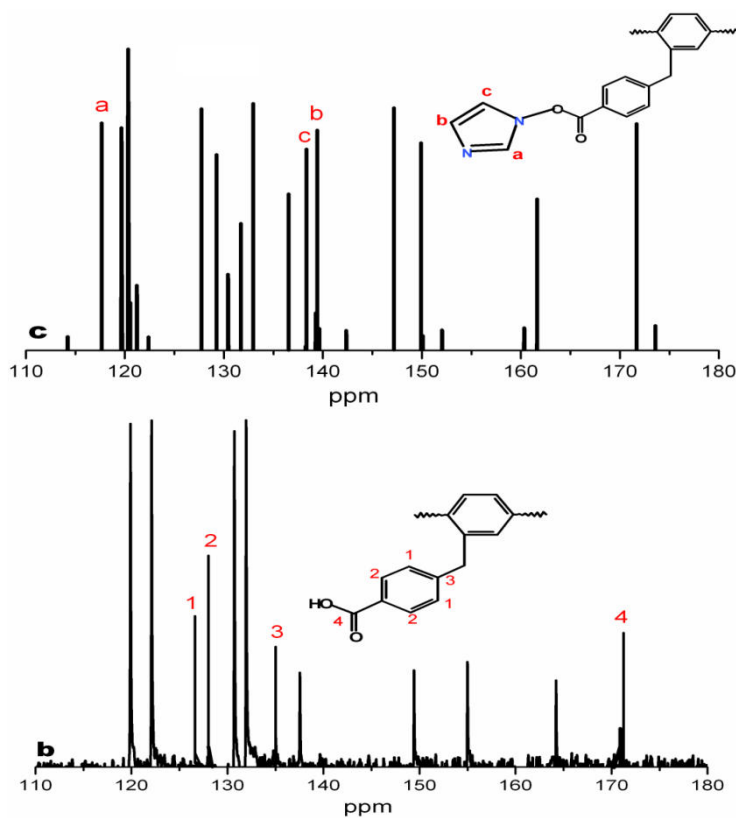


Figure3. ¹H NMR spectra of psf (a), mba-PSF (b) and imidazole-1-yl-4-methyl benzoate-PSF (c).



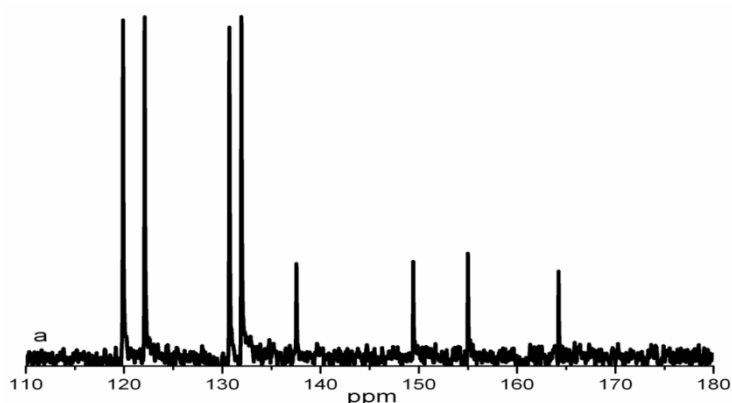


Figure 4 ^{13}C NMR spectra of psf (a), mba-psf (b) and imidazole-1-yl- 4 - methyl benzoate –PSF (c)

The activation energy for ion-migration (E_a) was estimated from the linear regression of $\log(\text{conductivity})$ vs. $1000T^{-1}$ as shown in Fig. 5, assuming an Arrhenius performance. The ion transport activation energy (E_a) for the polysulfones-imidazol-1-yl 4-methylbenzoate functionalizes membrane was calculated using the following equation;

$$E_a = -b \times R$$

Where b is the slope of the line regression of $\log(\text{Scm}^{-1})$ vs. $1000T^{-1} (\text{K}^{-1})$ plots, and R is the gas constant ($8.31 \text{ JK}^{-1} \text{ mol}^{-1}$). The E_a of the PSF - imidazol-1-yl 4-methylbenzoate membranes is 10.6 kJ mol^{-1} . These values are higher than the (E_a) of Nafion®-115 (6.00 kJ mol^{-1}). This shows that imidazole ion mobility in these membranes is more sensitive to temperature than proton migration in Nafion®-115.

The proton conductivity of membranes was well correlated with the temperature. As increasing the temperature, the proton conductivity of membrane was better.

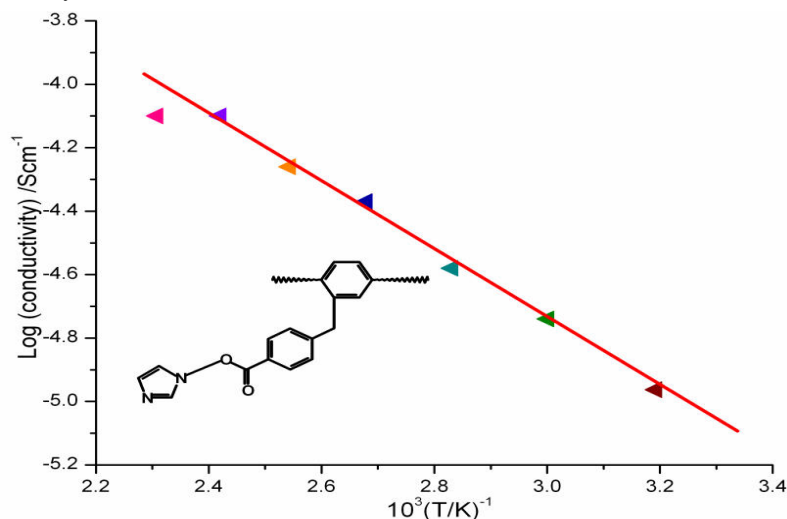


Figure 5. Temperature dependent anhydrous proton conductivity of imidazole-1-yl- 4 - methyl benzoate – PSF

The morphology of the psf-imidazol-1-yl 4-methylbenzoate membrane was studied and SEM images are presented in Fig. 6. The surface view of the membrane clearly shows a smooth and homogeneous membrane surface which indicates the infiltration of imidazole in polymer back bone is successfully.

The homogeneity of the surface of these membranes confirms that the polymer are dispersed well and there is no incompatibility among the materials used [29]. The degree of substitution (DS), i.e., the number of side chains per repeat unit of the PSF, was evaluated by integration and comparison of the ^1H NMR signals arising from the methyl protons at $\delta=1.6$ ppm and from the aromatic protons at $\delta=7.24\text{--}7.8$ ppm.

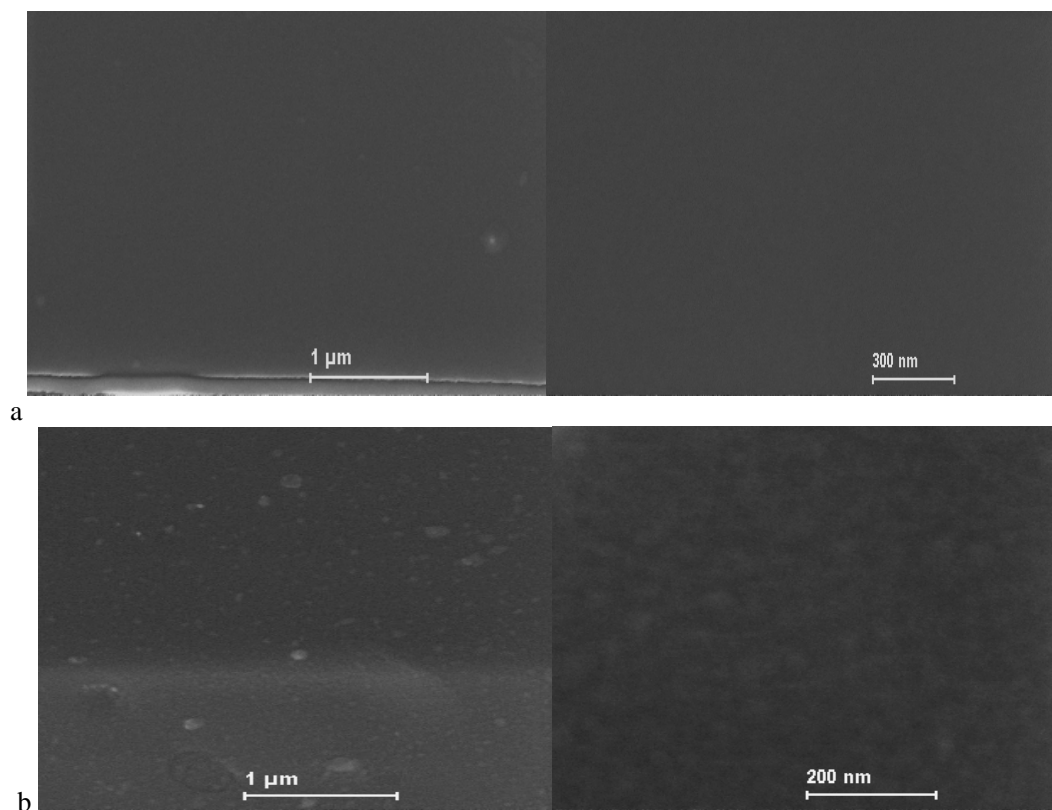


Figure 6 SEM analyses of 10% (a) and 5% (b) (v/w) of imidazole-1-yl-4-methyl benzoate –psf

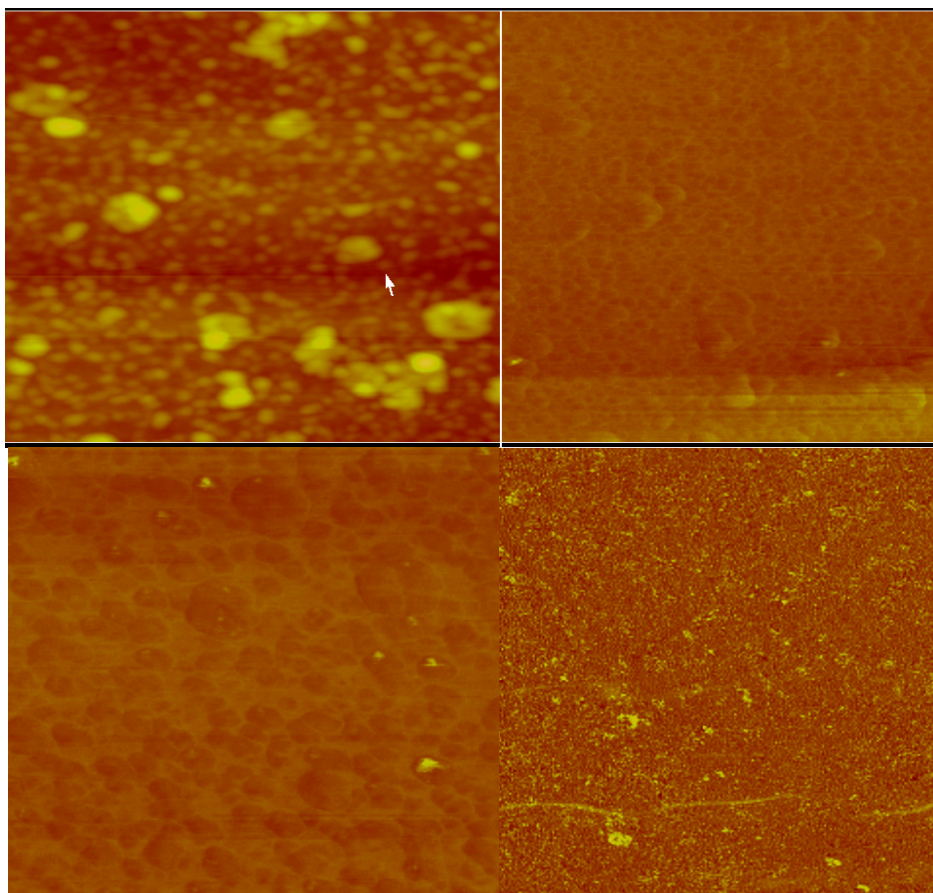


Figure 7 AFM analyses of imidazole-1-yl-4-methyl benzoate –PSF

5. CONCLUSION

In most cases, it was difficult to obtain more than one side chain per repeating unit of the polysulfone due to problems of reactivity connected with sterical hindrance and side reactions. We have prepared an anhydrous polymer electrolyte membranes material based on polysulfone ionomers with imidazole-1-yl-4-methyl benzoate units placed on pendent aromatic side chains by using an effectual two-step grafting procedure. Chloromethyl Benzoic acid ligand (CMBA) was bonded to the side chains of polysulfones (psf) giving aryl carboxylic acid-functionalized polysulfones via Friedal-Crafts reactions between polysulfones and chloromethyl benzoic acid and then imidazole was grafted on to benzoic acid through polymer reaction .

For controlling of the fabricated membrane properties, the number of side chains per repeat unit of PSF was achieved by adjusting of the experimental parameters. The chemical reaction between chloromethyl benzoic acid and imidazole was confirmed by NMR and FTIR to determine the degree of substitution. Such reaction imparted the membrane water uptake, swelling ratio, Ion Exchange Capacity and conductivity that strongly depended on the degree of substitution of imidazole.

The integrated imidazole moieties can be immobilized in the proton conducting membrane and can act as proton transporting media under elevated temperature with anhydrous conditions and increase the water uptake, and thus the conductivity. At high temperature the long-range proton transfer is induced by the structural reorganization of incorporated imidazole moieties and the proton conductivity increases with the temperature. The anhydrous proton conductivity of 7.94×10^{-5} s/cm at 160 °C related with the activation energy of 11.6 kJ mol⁻¹ for proton transport was observed. For the future work, in order to advance the fuel cell performance and stability, we are focusing on triazole and its derivatives to improving the mechanic strength of polymer backbones and adjusting local mobility of side chains, for the triazole-acids copolymers will be important and effective methods to reach the target.

ACKNOWLEDGMENTS

We acknowledge the financial supports for this work from National Natural Science Foundation of China (No. 51372192). The authors thank Ms. Xinmiao Liang from Prof. Jiwen Feng's Group at Wuhan Institute of Physics and Mathematics, Chinese Academy of Science, for NMR measurements.

Also I would like to thank all my colleagues in State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, for time they spent in teaching me how to use the various electrochemical devices in the laboratory and, for sharing me with some of his broad experience in the field of fuel cells research.

REFERENCES

- [1] Zhang, H.; Shen, P.K. (2012) Recent Development of Polymer Electrolyte Membranes for Fuel Cells. *Chem. Rev.* 2012, 112, 2780–2832.
- [2] D.S. Kim, Kim Ys), M.D. Guiver, B.S. Pivovar, (2008) *J. Membrane. Sci.* 321 199–208.
- [3] Shao, Y.; Yin, G.; Wang, Z.; Gao, Y. (2007) Proton Exchange Membrane Fuel Cell From Low Temperature To High Temperature: Material Challenges. *J. Power Sources*, 167, 235–242.
- [5] Weingartner, H.; Sasisanker, P.; Daguene, C.; Dyson, P. J.; Krossing, I.; Slattery, J. M.; Schubert, T. J. *Phys. Chem. B* (2007), 111 (18), 4775–4780.
- [6] Nakamura, K.; Shikata, T. (2010) *Chem phys* 11 (1), 285–294.
- [7] Bose, S.; Kuila, T.; Nguyen, T.X.H.; Kim, N.H.; Lau, K.-T.; Lee, J.H. (2011) Polymer Membranes For High Temperature Proton Exchange Membrane Fuel Cell: Recent Advances And Challenges. *Prog. Polym. Sci.*, 36, 813–843
- [8] Zhang, J. L et al. (2006). High Temperature Pem Fuel Cells. *Journal of Power Sources* 160, 872-891
- [9] Alberti, G. at al. (2006). Proton Conducting Membranes for Medium Temperature Fuel Cells: Recent Advances and New Strategies. *Desalination* 199, 4-5.
- [10] Cemil Dizman, Sahin Ates, Lokman Torun and Yusuf Yagci. 2010 Synthesis, Characterization and Photoinduced Curing of Polysulfones With (Meth) Acrylate Functionalities *Beilstein J. Org. Chem.*, 6, No. 56. Doi:10.3762/Bjoc.6.56
- [11] Vikas Mital. (Ed) (2011). *High Performance Polymer and Engineering Plastic*. Johnwiley and Sons
- [12] Juneau, J.; Mercier, R.; Gonon, L.; Gebel, G. *Macromolecules* 2007, 40, 983–990. Doi: 10.1021/Ma0614139.
- [13] Matsumoto, K.; Higashihara, T.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* 2009, 47, 3444–3453. Doi:10.1002/Pola.23403.
- [14] Stephen, R.; Gibon, C. M.; Weber, M.; Gaymans, R. J. *J. Polym. Sci., Part A: Polym. Chem.* 2009, 47, 3904–3913. Doi:10.1002/Pola.23457.
- [15] Yu, X.; Roy, A.; Dunn, S.; Badami, A. S.; Yang, J.; Good, A. S.; Mcgrath, J. E. 2009 *J. Polym. Sci., Part A: Polym. Chem.*, 47, 1038–1051. Doi:10.1002/Pola.23194.
- [16] Filimon, A.; Avram, E.; Dunca, S.; Stoica, I. & Ioan, S. (2009). Surface Properties and Antibacterial Activity of Quaternized Polysulfones. *Journal of Applied Polymer Science*, Vol.112, No.3, (February 2009), Pp. 1808-1816, ISSN 1097-4628.
- [17] Benoît Lafitte. 2007, Proton-Conducting Sulfonated and Phosphonated Polymers and Fuel Cell Membranes By Chemical Modification Of Polysulfones. Division of Polymer & Materials Chemistry Lund University Doctoral Thesis.
- [18] Petreus, O.; Avram, E. & Serbezeanu, D. (2010). Synthesis and Characterization of Phosphorus-Containing Polysulfone. *Polymer Engineering Science*, Vol.50, No.1, (January 2010), Pp. 48-56, ISSN 1548-2634.
- [19] Zicheng Zuo, Yongzhu Fu and Arumugam Manthiram (2012). Novel Blend Membranes Based On Acid-Base Interactions for Fuel Cells. *Polymers* 2012, 4, 1627-1644; Doi: 10.3390/Polym4041627.
- [20] Zhen zhou (2007). Development of Polymer Electrolyte Membranes for Fuel Cells to be operated at High Temperature and Low Humidity. Georgia Institute of Technology Copyright © 2007 by Zhen Zhou.
- [21] Subbaraman, R.; Ghassemi, H.; Zawodzinski, T. (2009), Triazole and Triazole Derivatives as Proton Transport Facilitators in Polymer Electrolyte Membrane Fuel Cells. *Solid State Ionics* 180, 1143–1150.

- [22] Kim, J.-D.; Oba, Y.; Ohnuma, M.; Jun, M.-S.; Tanaka, Y.; Mori, T.; Choi, Y.-W.; Yoon, Y.-G. Physico (2010). Chemical Properties of Highly Flexible Temperature Tolerant Anhydrous Nafion-1, 2, 3-Triazole Blend Membranes. *J. Electrochem. Soc.*, 157, B1872–B1877.
- [23] P. Tölle, W. L. Cavalcanti, M. Hoffmann, C. Köhler, and T. Frauenheim. Modelling of Proton Diffusion In Immobilised Imidazole Systems for Application in Fuel Cells. *Fuel Cell* DOI: 10.1002/Fuce.200800006.
- [24] Jailakshmi Krishnamurthy, Leon Dyers. Jr. and John B.Kerr. 2012 Imidazole Tethered Polymers As Anhydrous Proton Conducting Membranes For High Temperature PEM Fuel Cells 2010 [Http://Ecsdl.Org/Site/Terms_Use](http://Ecsdl.Org/Site/Terms_Use).
- [25] Schuster, M., Rager, T., Noda, A., Kreuer, K. D.& Maier, J.(2005) About the choice of the protogenic group in PEM separator materials for intermediate temperature, low humidity operation: A critical comparison of sulfonic acid, phosphonic acid and imidazole functionalized model compounds. *Fuel Cells* 5, 355-365 (2005).
- [26] Y.S. Kim, L. Dong, M.A. Hickner, T.E. Glass, V.Webb, J.E. Mcgrth, *Macromolecules* 36 (2003) 6281–6285.
- [27] S. Gottesfeld, T. A. Zawodzinski.1997, *Adv. Electrochem. Sci.Eng.* 1997, 5, 195.
- [28] R.A. Meyers (Ed.) (2000). Interpretation of Infrared Spectra, A Practical Approach. *Encyclopedia of Analytical Chemistry*. John Wiley & Sons Ltd
- [29]Suryani, Y. Chang, J. Lai and Y. Liu,(2012) *Journal of Membrane Science*, 403 (2012) 1.