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Polyimide based polymer electrolyte membranes containing polyrotaxane for direct methanol fuel cell applications

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Abstract — *Proton exchange membranes (PEMs) consisting of polyimide (PI) and polyrotaxane (PR) were developed for direct methanol fuel cell applications under 100% relative humidity (RH). PEMs were prepared by the solution casting technique. The morphology, thermal and mechanical properties of the membranes was investigated by SEM, TGA, and tensile strength test, respectively. Also, the prepared membranes were systematically characterized in terms of ion exchange capacity, water uptake, methanol uptake, swelling behavior and proton conductivity. Besides X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR) was used to confirm the structural modifications of polymer electrolyte membranes. With the addition of PR into PI polymer, the blend membrane exhibits a conductivity value in the order of 10^{-1} Scm^{-1} at 70 °C temperature and at 100% relative humidity. This developed membrane shows good prospect as a proton exchange membrane in fuel cell applications.*

Keywords- *Polymer electrolyte membranes; Proton conductivity; Polyimide; Polyrotaxanes; Direct methanol fuel cell*

I. INTRODUCTION

Direct methanol fuel cell (DMFC) is a promising candidate for high-energy-density portable power sources [1]. However, the major problem encountered by DMFC is its low performance and high cost. Nafion, a commercially available polymer electrolyte membrane (PEM) developed by DuPont, has been used in fuel cell, because this perfluorinated ionomer membrane has a high chemical and electrochemical resistance as well as high proton conductivity, but they suffer from the issues of high methanol permeability, high cost and environmental inadaptability[2, 3]. Therefore, extensive research efforts have mainly been focused on developing an alternative low-cost membrane that decreases the crossover of methanol through PEMs while maintaining good proton conductivity.

Different methods are being explored in improving the proton conductivity without sacrificing mechanical strength or vice versa. Various attempts like copolymerization, grafting, polymer blending or crosslinking are considered as efficient approaches in developing PEMs in DMFCs. The most current development strategies use modified PFSA polymers, acid-functionalized aromatic hydrocarbon-based polymers or a number of sulfonated aromatic polymers [4]. The selection of polymers for PEMs of DMFCs is very important because proton conductivity and methanol permeability properties largely depend on the polymers.

In the present study, we have adopted blending technique, because of its ease in preparation and easy control of physical properties within the compositional regime. Polyimides have been investigated as potential PEM materials by several groups [5, 6] and have shown promising attributes in terms of their low methanol crossover and sufficient conductivity due to their excellent mechanical and thermal properties. Polyrotaxanes - poly (ethylene glycol) (PEG) mechanically interlocked into α-CD cavities, have become increasingly interesting nowadays due to their numerous practical applications [7]. We selected polyimide (PI) as a matrix polymer and polyrotaxane as a blending or doping polymer network. The membranes were prepared by a solution casting method from PI and PR solutions, and the characteristics of the resulting solution-cast PI/PR blend membranes as PEMs for DMFCs were investigated.

II. EXPERIMENTAL

A. Membrane Preparation

Polyimide (PI) (Otto Chemi), Poly (ethylene glycol) (PEG) (SRL Industries), α- Cyclodextrin (α- CD) hydrate (Alfa Aesar), m-Cresol (Loba), N, N – Dimethyl sulfoxide (DMSO) (Merck) were the chemicals (AR grade) used without further purification in this study. The polyrotaxane composed of α-cyclodextrin and poly(ethylene glycol), was prepared according to a work reported previously [3]. The polymer electrolyte membranes were prepared by solution casting technique. Appropriate weight ratio of PI and PR polymer were dissolved in m-Cresol and DMSO respectively and the solutions were mixed together and casted in Petri dish and then dried to form a blend membrane.

B. Membrane Characterization

XRD patterns of PI blend membranes were obtained with a PANalytical X'Pert diffractometer and Fourier transform infrared (FT-IR) spectra was recorded using a Bruker spectrometer. A typical SEM image was obtained from FEI Quanta 200 electron microscope for analyzing the morphology of surfaces. Mechanical strength of membranes was measured with a Uniaxial tensile testing machine, Instron 3345, UK. The samples were measured at a strain rate of 2 mm/min. Thermal analysis was performed by means of a NETZCH Germany & STA 449 F3 Jupiter instrument (nitrogen flux; temperature interval: 30 °C to 600 °C; heating rate: 10 °C/min). The AC impedance spectra were recorded using CH Instruments 600D series electrochemical analyzer at frequencies between 1 kHz and 1 MHz and temperatures from 30 °C to 70 °C with the applied amplitude of 10 mV from 1 KHz to 10 MHz. The ion exchange capacity (IEC), liquid uptake and swelling ratio were performed in accordance with our previous reports [8].

III. RESULTS AND ANALYSIS

A. Structural and morphological analysis

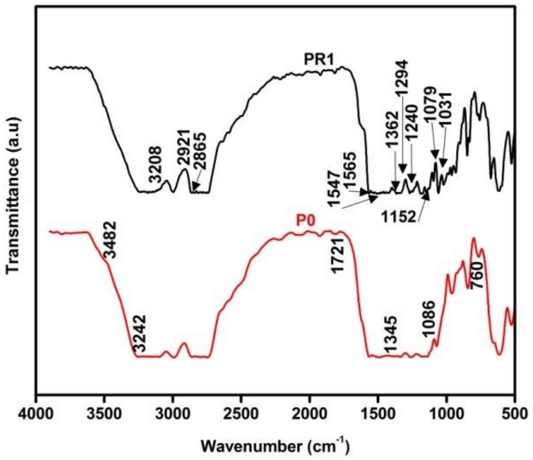

Figure 1. FTIR spectra of pure PI and PI/PR blend membranes

Fig. 1 shows the FTIR spectra of pure PI and PI with 10 wt % PR blend membranes. Typical absorption bands for polyimide are found at 1721cm^{-1} (C=O, symmetric) 1345cm^{-1} (C–N, asymmetric) [9]. The absorption band assigned to the O-H stretching vibration was observed in the range of 3600–3200 cm^{-1}. The PI/PR spectrum shows the characteristic bands of the α-CD macrocycle at 2921 cm^{-1} (C-H stretching vibration) 1152-1030 cm^{-1}(C-O-C stretching), 1240-1041 cm^{-1} (C-O-C stretching) and 2865 cm^{-1} (C-H stretching vibration of PEG) [10]. The amide II band (N-H vibration) emerges at 1547 and the methyl groups at 1362 cm-1 [11].

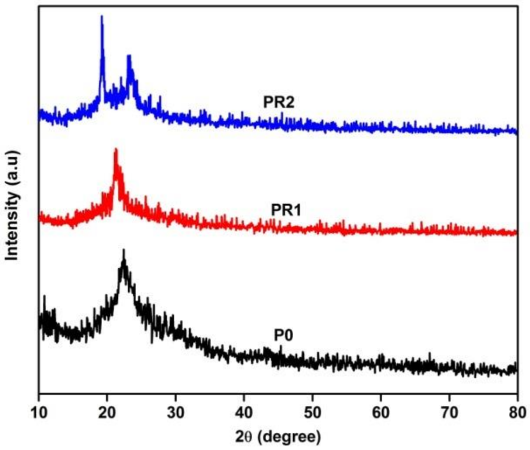

Figure 2. X-ray diffraction (XRD) spectrum of the polyimide and blend films

In the diagrams for the polyrotaxanes (Fig. 2), the characteristic reflection of the structure clearly appears. The results indicate that the polyrotaxanes contained crystalline inclusion complex domains that were isomorphous with the channel-type structure formed by the α-CD-PEG inclusion complex [12]. The patterns of the polyrotaxanes are broadened, indicating that the polyrotaxanes had low crystallinity due to the macromolecular nature and the presence of amorphous PEG segments in the polyrotaxanes. The pattern of the polyrotaxane exhibit a strong peak at 2θ = 20.11. This is the characteristic diffraction peak that form a channel-type crystalline structure of polyrotaxane or inclusion complex

[11]. It can be seen that the main broad diffraction peaks of all the membranes appeared at 2θ (22.52°, 21.26° and 19.26°). Besides, the diffraction peaks appeared at 23.26° in PR2 blend film [13].

The scanning electron micrograph of the PI with 10% PR blend membranes is shown in Fig. 3. with different magnifications (200× and 5,000×). The micrograph depicted simple flakes morphology with randomly dispersed regions. As can be seen in the figures, the distribution of polyrotaxane particles is relatively uniform in the polymer matrix. This means that the membranes were successfully prepared.

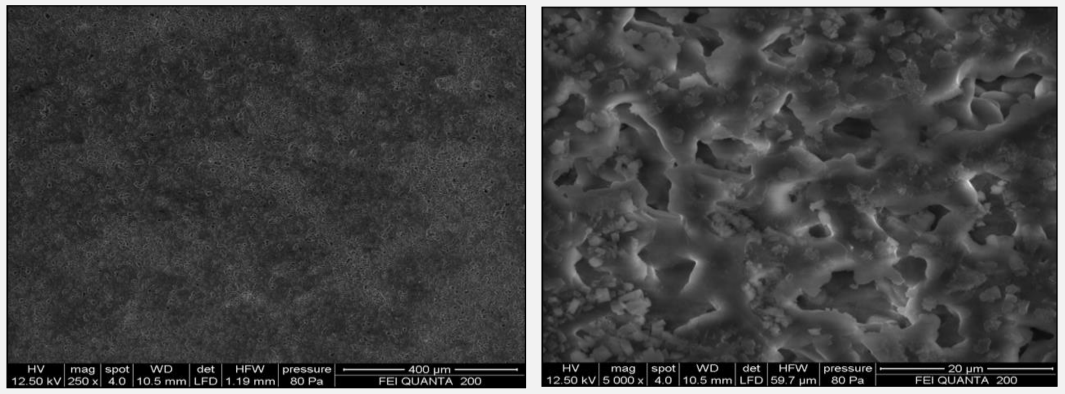

Figure 3. SEM images for PR 10% sample at (200× & 5,000×) magnifications

B. Thermal and Mechanical Analysis

Table 1. TGA results for different PEMs

Membrane	**$T_{10\%}$ (˚C)**	**$T_{50\%}$ (˚C)**	**T_{max} (˚C)**	**Residual Weight (mg) at 600˚C**
P0	419	462	483	3.80
PR1	414	460	484	6.64
PR2	367	454	490	3.70

The thermal stability of the prepared samples was measured using thermo-gravimetric analyzer (TGA). In this technique, the weight loss of the material due to the formation of volatile compounds under degradation due to heating and rise in temperature is monitored. The data available from TGA is tabulated in Table 1 and graphed in Figure 4, this includes $T_{10\%}$ (onset temperature), the temperature at which 10% degradation from the sample occurs, $T_{50\%}$, the temperature at which 50% degradation occurs, T_{max}, the temperature at which maximum degradation occurs, and residual loss at 600˚C.

According to TGA results as shown in Figure 4, the incorporation of PR to PI improved the thermal stability at higher degradation temperature ranges compared to pure PI. The temperature of the 10% degradation of PR 10% and PR 20% has been shifted to lower temperatures relative to PR 0%. The maximum degradation temperatures have been shifted to higher temperatures compared to PR 0%. This means that, thermal stability has been occurred with increase in the concentration of PR compared to PI. The residual weight of the samples at 600˚C decreased with increasing the concentration of PR blend to PI. Thus, thermal stability of PI/PR has been improved slightly compared to pure PI.

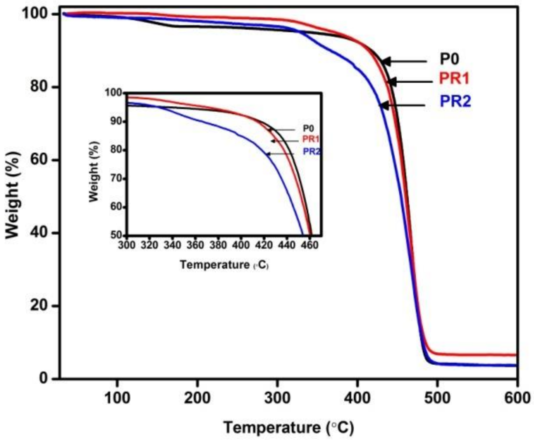

Figure 4. TGA curves for pure PI and PI/PR blend membranes

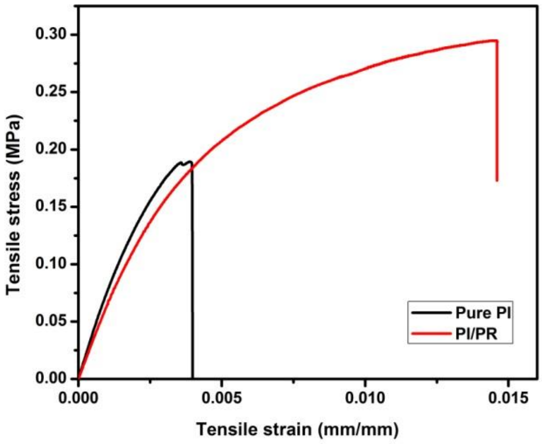

Figure 5. Curves of tensile strength vs. strain

The tensile property improvements of PI/PR blendes are plotted in Fig. 5. The typical stress-strain curves of PI/PR blendes which exhibit superior mechanical properties compared to that of pure PI films are shown in Fig. 5. The tensile strength of the PI/PR film containing 10 wt% of PR loading is 0.29225 MPa which is higher than that of pure PI film. Meanwhile, the elongation at break of PI/PR film containing 10 wt% PR loading is 3.66026 mm, which is about 33.2% greater than that of pure PI film. The data in Fig. 5 indicates that the slight mixing of PR (10 wt%) into PI matrix can greatly improve the mechanical properties of the PI/PR blend. More importantly, small amount of PR mixing exhibits improved mechanical property of PI, thereby reducing cost in practical applications.

C. Ion Exchange Capacity, Liquid Uptake and Swelling of membrane

Table 2. The IEC, liquid uptake, swelling ratio and proton conductivity of the polymer electrolyte membranes

Membrane	IEC (meq/g)	Water uptake (%)	Swelling ratio (%)	Methanol uptake (%)	Proton conductivity (Scm^{-1})		
					30 °C	50 °C	70 °C
P0	0.79	7.71	8.3	26.33	0.011	0.033	0.034
PR1	1.85	11.8	9.8	18.2	0.026	0.036	0.044
PR2	0.96	14.3	10.7	12.5	0.014	0.021	0.030

The IEC, water uptake, methanol uptake and swelling ratio of the prepared blend polymer electrolyte membranes are tabulated in Table 2. The IEC of the PI membrane is 0.79 meq. g^{-1} and this value increases with the amount of PR inside the membrane. Both of the swelling and water uptake showed a similar trend with IEC values. The higher water uptake and swelling ratio exhibited by the PR2 membrane were 14.3 % and 10.7 % respectively. An increased swelling of the membrane increases the free volume for diffusion across it for hydrated protons, which therefore affect the proton conductivity [14]. The methanol uptake of the PI/PR blend membranes decreased with increasing amounts of PR. The membrane PR1 shows a favorable methanol uptake value of 12.5 %.

D. Proton Conductivity

The proton conductivity values of the blend membranes are tabulated in Table 2 and shown in Fig. 6. The performance and the efficiency of the fuel cell depend on the proton conductivity. Generally, the proton conductivity and the water uptake of the membrane directly depend on the IEC of the polymer. The proton conductivity of PI/PR membranes increased for up to 10 wt% PR, and then decreased for larger amounts of PR. The addition of PR significantly increases the hydrophilicity of the membrane, and thus the presence of water keeps it hydrated and maintains the proton conductivity. The crystallinity decreased with the addition of PR, implying improved water transport and swelling [3, 15, 16]. Obviously the enhanced water uptakes of the membranes contribute to proton mobility through the membrane. The conductivity was maximal for a membrane containing 10 wt% PR with 90 wt% polyimide.

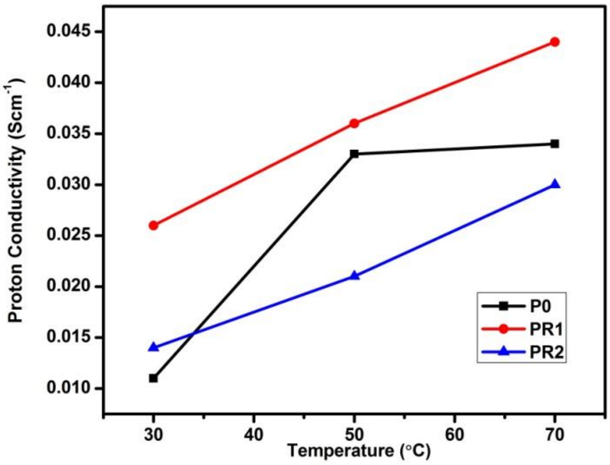

Figure 6. Proton conductivity of PI and the blend membranes as a function of temperature

IV. CONCLUSIONS

A series of polyimide and polyrotaxane blend membranes have been prepared by solution casting method and characterized. The effects of varied weight ratios of polyrotaxane on polyimide ion exchange capacity, water uptake, methanol uptake, proton conductivity were studied at various temperatures. The synthesized PI/PR blend membrane shows better mechanical properties. Relatively high proton conductivity values were achieved and it was shown that they were dependent on ion exchange capacity and temperature. The introduction of polyrotaxane into the polymer blend may have assisted in the proton transfer mechanism. At 70 °C, the proton conductivity of the PR1 membrane exhibited 0.044 S cm^{-1} under 100% RH condition. Therefore, considering these results, it is expected that these blend membranes will deliver excellent performance in fuel cell systems in near future.

REFERENCES

[1]. Kamarudin S K, Achmad F, Daud WRW, “Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices”, *International Journal of Hydrogen Energy*, 34, pp. 6902–6916, 2009.

[2]. Ranjan K. Mallick, Shashikant B. Thombre, Naveen K. Shrivastava, “Vapor feed direct methanol fuel cells (DMFCs): A review”, *Renewable and Sustainable Energy Reviews*, 56, pp. 51–74, 2016.

[3]. Hyun Dong Cho, Jongok Won, Heung Yong Ha, “Composite polymer electrolyte membranes containing polyrotaxanes”, *Renewable Energy*, 33, pp. 248–253, 2008.

[4]. Yun-Sheng Ye, John Rick and Bing-Joe Hwang, “Water Soluble Polymers as Proton Exchange Membranes for Fuel Cells”, *Polymers*, 4, pp. 913-963, 2012.

[5]. Jingling Yan, Xiaoming Huang, Hunter D. Moore, Chao-Yang Wang, Michael A. Hickner, “Transport properties and fuel cell performance of sulfonated poly(imide) proton exchange membranes”, *International Journal of Hydrogen Energy*, 37, pp. 6153-6160, 2012.

[6]. Lei Geng, Yao He, Dan Liu, Xin Dai, Changli Lü, “Facile in situ template synthesis of sulfonated polyimide / mesoporous silica hybrid proton exchange membrane for direct methanol fuel cells”, *Microporous and Mesoporous Materials*, 148, pp. 8-14, 2012.

[7]. Harada, Akira; Li, Jun; Kamachi, Mikiharu, “The molecular necklace: a rotaxane containing many threaded α-cyclodextrins”, *Nature*, 356 (6367), pp. 325-327, 1992.

[8]. Sainul Abidin, K. Kannan, R. Bahavan Palani, P. and Rajashabala, S. “Role of structural modifications of Montmorillonite, electrical properties effect, physical behavior of nanocomposite proton conducting membranes for Direct Methanol Fuel Cell applications”, *Materials Science-Poland*, DOI: 10.1007/s11581-014-1193-1, 2017.

[9]. Huiping Bi, Jiali Wang, Shouwen Chen, Zhaoxia Hu, Zhilin Gao, Lianjun Wang, Ken-ichi Okamoto, “Preparation and properties of cross-linked sulfonated poly(arylene ether sulfone)/sulfonated polyimide blend membranes for fuel cell application”, *Journal of Membrane Science*, 350, pp. 109-116, 2010.

[10]. Ana-Maria Resmerita, Khaleel I. Assaf, Alexandra I. Lazar, Werner M. Nau, Aurica Farcas, “Polyrotaxanes based on PEG-amine with cucurbit[7]uril, α-cyclodextrin and its tris-*O*-methylated derivative”, *European Polymer Journal*, 93, pp. 323-333, 2017.

[11]. Huaiqing Yu, Zeng-guo Feng, Ai-ying Zhang, Dandan Hou, Ling-gang Sun, “Novel triblock copolymers synthesized via radical telomerization of N-isopropylacrylamide in the presence of polypseudorotaxanes made from thiolated PEG and α-CDs”, *Polymer*, 47 pp. 6066-6071, 2006.

[12]. Chuan Yang, Xiping Ni, Jun Li, “Synthesis of polyrotaxanes consisting of multiple α-cyclodextrin rings threaded on reverse Pluronic PPO-PEO-PPO triblock copolymers based on block-selected inclusion complexation”, *European Polymer Journal*, 45, pp.1570-1579, 2009.

[13]. Shuwei Zhou, Jingwen Wang, Gaoqiang Wang, Zhi Jiang, Hua Ren, “An approach to developing high dielectric constant nanocomposites based on polyrotaxane derivative”, *European Polymer Journal*, 90, pp. 312–322, 2017.

[14]. Hyun Dong Cho, Jongok Won, Heung Yong Ha, Yong Soo Kang, “Nafion Composite Membranes Containing Rod-Shaped Polyrotaxanes for Direct Methanol Fuel Cells”, *Macromolecular Research*, 14 (2), pp. 214-219, 2006.

[15]. Jongok Won, Hyun Dong Cho, Yong Soo Kang, “The Effect of Annealing on sSEBS/Polyrotaxanes Electrolyte Membranes for Direct Methanol Fuel Cells”, *Macromolecular Research*, 17 (10), pp. 729-733, 2009.

[16]. Ji Hwan Son, Yong Soo Kang, Jongok Won, “Poly (vinyl alcohol)-based polymer electrolyte membranes containing polyrotaxane”, *Journal of Membrane Science*, 281, pp. 345-350, 2006.