Analytical & Bioanalytical Electrochemistry

> 2023 by CEE www.abechem.com

Full Paper

New Proton Exchange Membrane Blends based on Polybenzimidazole and Poly(1,4- Phenylene Ether Ether Sulfone) for Fuel Cells Application

Parvaneh Kakavand,^{1,2} Zahra Mokhtari,^{1,2} Mehran Javanbakht,^{1,2,*} and Khadijeh Hooshyari³

¹Department of Chemistry, Amirkabir University of Technology, Tehran, Iran ²Renewable Energy Research Center, Amirkabir University of Technology, Tehran, Iran ³Department of Applied Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran

*Corresponding Author, Tel.: +982164545806 E-Mail: <u>mehranjavanbakht@gmail.com</u>

Received: 24 April 2023 / Received in revised form: 5 June 2023 / Accepted: 7 June 2023 / Published online: 30 June 2023

Abstract- To develop proton exchange membrane blends based on polybenzimidazole (PBI), a novel polymer blend membrane consisting of PBI and sulfonated poly 1,4-phenylene ether ether sulphone (SPEES) was prepared by solution casting method. The goal of the work was to study the performance of the acid-base composition on its properties, such as mechanical stability, thermal stability, and proton conductivity of PBI-SPEES blend membranes. The N–H…O interactions between the PBI and SPEES in the blend membranes indicated that the two polymers form a miscible blend. The acid uptake (12 moles) and proton conductivity (101 mS/cm in 160 °C) of the blend membranes were significantly ameliorated as compared to pure phosphoric acid-doped PBI (APBI) membranes. A single glass transition value of PBI-SPEES blend membranes which were between the glass transition value of the PBI and SPEES membranes confirmed the miscible properties of PBI-SPEES blend membranes. The presence of SPEES in the blend membranes decreases the friability and hardness and increases the flexibility and proton conductivity of APBI membranes. According to the PEM fuel cell results, with a high-power density of 0.65 W/cm2 at 180 °C, the PBI-SPEES blend membranes have a high potential for use as an appropriate membrane in the fuel cells.

Keywords- Proton exchange membrane; Polybenzimidazole; Sulfonated poly 1,4-phenylene ether sulphone; Miscible blends

Fuel cells provide a new technology that generates electricity by chemical reaction [1,2]. Proton Exchange Membrane (PEM)-based fuel cells serve as one of the most encouraging technologies for clean energy [3,4]. The PEM fuel cells are currently being used as devices of energy conversion with certain advantages, including high-energy density, low-cost preparation conditions, high-speed setup, and high efficiency [5,6]. Nation is a high commercially substance serving as a polymeric membrane in PEM fuel cells since having great mechanical, chemical, and thermal stabilities, as well as high proton conductivity [7,8]. Nonetheless, it still suffers from the high expense and low proton conductivity and stability under high operating temperatures so unable to provide all the required conditions of the PEM fuel cells [9]. Improvement of High-Temperature Proton Exchange Membrane (HT-PEM) fuel cells to dissolve the difficulties of current cells based on Nafion is rather ambitious [10-13]. Therefore, a lot of efforts have been made to create HT-PEMs that are capable of conducting protons under temperatures as high as 180 °C [14-19]. Higher work temperatures increase cell efficiency, electrolytic reaction, CO tolerance, faster electrode kinetics and it's also easy to manage water and heat [20-24]. Much effort has been made for developing PEMs under temperatures over 100°C. For this purpose, developed membranes be divided into four major groups [25-27]: 1) Sulfonated polymer and composite membranes derived from them, 2) organic-inorganic composite membranes, 3) acid-base polymer membranes, and 4) Nafion membranes modified. Among the aforementioned membranes, acid-base-based PEMs have been studied extensively as suitable candidates to be used in HT-PEM fuel cells because of their outstanding electrochemical properties like excellent proton conductivity and high efficiency in high temperatures and conditions without water [28,29]. Phosphoric Acid (PA)doped polybenzimidazole (PBI) (APBI) membranes have attracted much attention during the past few years while being the best option for Nafion to carry out a high-temperature operation to date. The APBI membranes exhibit high mechanical stability, as well as high proton conductivity under temperatures of over 200 °C. Also, there are several other benefits like low gas penetrability, good thermal and oxidative stabilities, and a near-zero water drag coefficient. Proton transfer from the APBI membrane depends on the PA doping level [30]. Polymer blending is a potentially convenient approach to producing novel polymeric materials with chemical and/or physical properties by providing a mixture of two or more polymers of diverse physical properties. Blending acidic and basic polymers can reinforce mechanical abilities without weakening their other features which would minimize the unfavorable swelling and increase the stability of the material. New beneficial development polymer blend membranes can be effective for the development of unaffected mechanically strong membranes with high proton conductivity and excellent thermal stability [31,32]. The PBI membranes have been reported to be ionically crosslinked by mixing PBI (comprising basic atoms of nitrogen) with various sulfonated polymers serving as an acidic component). In a series of papers, has been

reported better PBI properties (especially proton conduction behavior) upon blending with a variety of polymers, including sulfonated poly(ether ether ketone), poly-(vinylidene fluorideco hexafluoropropene), sulfonated poly(sulfone), poly(vinylidene fluoride), sulfonated polystyrene, sulfonated poly(aryl ether ether ketone), sulfonated poly(acrylic acid) polysulfone and sulfonated poly(ether ketone). The prepared PBI base blend membranes display excellent proton conductivity, suitable thermal stability, reasonable mechanical strength, and therefore the performance of the fuel cell is good [33-38]. The influences of the Degree of Sulfonation (DS) of sulfonated polymers on the mechanical stability and proton conductivity of PEMs have been studied as an important parameter [39,40]. Poly 1,4-phenylene ether sulphone (PEES) is well known for providing good properties in film-formation, high thermal resistance, as well as proper stability in acidic conditions [41,42]. So, Sulfonated PEES (SPEES) serves as a potential PEM substance in fuel cells. The PBI is a macromolecule with hydrogen bond sites of proton acceptor (-N=) and donor (-NH-) that may form miscible blends that specifically interact with a variety of polymers. The required molecular strength and rigidity, associated with proper processability are provided via aromatic and ether linkages in the SPEES structure. The SPEES is a rather novel material already employed in the area of membrane technology [10].

In the present work, new PBI- and SPEES-based blend membranes were prepared with a different percentage of the weight of SPEES. PBI and SPEES were used as the basic polymer and second polymer respectively. The PBI-SPEES blend membranes showed high thermal and mechanical stabilities and excellent proton conductivity. The blend membranes were studied in terms of proton conductivity, miscibility, and thermal stability through thermal and electrical approaches based on spectroscopic techniques. They were further investigated in terms of morphology via microscopic techniques to delineate microstructure effects on their properties.

2. EXPERIMENTAL SECTION

2.1. Materials

Polybenzimidazole was obtained by the Fuma Tech company. N,N-dimethylacetamide, and phosphoric acid (DMAc) were bought from Merck. Distilled deionized water (DI) was used in all the tests. Poly (1,4-phenylene ether ether sulfone), PEES, pellets (Tg = 192 °C) was supplied by Aldrich. Other reagents with high quality were obtained by KimiaGohar (Tehran, Iran).

2.2. Sulfonation of SPEES

Sulfonation (PEES) was performed by slightly modifying the method of Unveren et al. [10,43]. Twenty-five grams of dried PEES in 95-98% concentrated sulfuric acid was prepared and then stirred at 400 rpm for different periods (1.5, 2.5, 3.5, 4, 5, 6, and 7 h) In conditions at the reaction temperature, Under nitrogen with a robust mechanical instigation. After achieving

the reaction time, gradual precipitation of the reaction mass in the cold ice water was followed. The product was filtered several times to neutralize the pH. This swollen mass was dried in a vacuum first at room temperature for 24 h and then at 60 °C for 12 h to obtain the SPEES. The DS of prepared SPEES polymers from the following equation was calculated (1):

$$DS = \frac{\left[0.324 \times C_{NaOH} V_{NaOH}\right]}{\left[W - 0.08C_{NaOH} V_{NaOH}\right]} \tag{1}$$

where C_{NaOH} represents NaOH solution molarity (M); V_{NaOH} demonstrates NaOH volume (mL) consumed for neutralizing the polymer solution; W is the solid polymer weight (g); and the molecular weight of PEES at each repeated unit and the difference between the molecular masses of PEES and SPEES are shown to be 324 and 80, respectively. The prepared SPEES polymer is named SPEESx, where x represents the DS of SPEES polymer. The SPEES was produced with various DS, and the membrane was prepared by selecting the optimal DS of 68%.

2.3. Preparation of blend membranes

The blend membrane of high proton conductivity was prepared by choosing SPEES with 68% DS. Preparation of the blend membranes was followed by mixing PBI with SPEES polymers in DMAc by using the solution-casting method. PBI powder was solved in DMAc in a nitrogen atmosphere at 150 °C. Then, varied SPEESx contents (SPEESx/PBI weight ratio: 5, 10, 15, 20, and 25) were added to the PBI solution at room temperature, and mixing at this temperature was followed for 2 days with stirring by a magnetic stirrer. A polytetrafluoroethylene (PTFE) cell membrane of 0.2 μ m was used for filtering the homogeneous solutions of the blended films, which were then cast after pouring them into a clean glass Petri dish at a temperature of 80 °C. Before being immersed in PA, blend membranes of PBI-SPEESx are called PBISx-y, in which x and y represent the weight percentages of SPEES polymer vs. dry PBI polymer and DS of SPEES polymer, respectively. These membranes after immersion in PA named APBISx-y.

2.4. Characterization techniques

Using a single-reflection Bruker Equinox 55 FT-IR spectrometer, Fourier transform infrared (FT-IR) spectra (4000-400 cm⁻¹, resolution 4 cm⁻¹) of the thin blend films (~70 μ m) were recorded through Attenuated Total Reflectance (ATR) spectrometry with an average of 64 scans. Thermogravimetric analysis (TGA) was conducted in flowing nitrogen (25-800 °C) at the scanning rate of 10 °C/min via a TA Instruments TGA-2050 system. The glass transition temperatures (T_g) of the blend samples were studied by using a differential scanning calorimetry (DSC) device (DSC Q-10, TA instruments). The samples in flowing nitrogen (25-800 °C) were maintained at a heating rate of 10 °C/min. were on A Philips PW-1700

diffractometer with a rotating anode ($l = 1.5418 \text{ A}^{\circ}\text{w}$, Cu Ka) was employed to perform X-ray diffraction analyses. The morphology of the blend membranes was studied via Scanning Electron Microscopy (SEM) (Model JSM-5600, Joel Co). The mechanical properties of the blend membranes were measured on an Instron 5543A tensile test machine. The sample size and elongation rate at room temperature were 7-1 cm² and 10 mm min⁻¹, respectively.

2.5. Membrane characterization

2.5.1. Ion exchange capacity (IEC)

The IEC of the membranes was specified via the titration method. Immersion of the membranes in 2 M NaCl solutions was done at 25 °C for 24 h. The solutions were titrated with 0.1 M NaOH, with which phenolphthalein was used as an indicator. Calculation of the IEC (meq/g) value was done by using the following equation (2):

$$IEC = \frac{(V_{NaOH})(M_{NaOH})}{W_{Dry}}$$
(2)

where V_{NaOH} denotes the consumed NaOH volume (mL) in the titration; M_{NaOH} stands for NaOH molarity; and W_{Dry} shows the dry weight (g) of the membrane.

2.5.2 PA doping level (PA_{dop})

The PA_{dop} of the membranes was calculated as the number of PA moles of obtained for 1 mol of the repeated unit of PBI. Doping level was performed by immersing the dry membranes in aqueous phosphoric acid (85 wt.% of PA) for 5 days. The doped membranes, which were dried in a vacuum oven at 60°C for 24 h to separate the water content from the doping acid and doping level, were defined by finding the weight of the acid absorbed by the membranes. The results obtained from Equation 3 were applied for calculating the PA_{dop} of the membranes.

$$PA_{dop} = \frac{\left[\begin{pmatrix} W_1 - W_0 \end{pmatrix} / M_w \text{ of } PA \right]}{\left[\begin{matrix} W_0 \\ M_w \text{ of } PBI \text{ repeat unit} \right]}$$
(3)

2.5.3. Proton conductivity measurements

Measurement of the proton conductivity of the membranes was done by using the fourpoint probe method in dry conditions. An impedance analyzer was utilized with a PGSTAT 303N potentiostat/galvanostat (Ecochemie) to measure the impedance of the membranes in the frequency domain of 1-100 Hz. The acid-loaded membrane was mounted onto the test cell. The proton conductivity was calculated via the following equation (4):

$$\sigma = \frac{L}{RWT} \tag{4}$$

where σ is proton conductivity (S/cm) and L is the spacing of electrodes T and W, representing the thickness and width of the blend membranes, respectively. In all the cases, R was obtained from the Nyquist plot.

The Arrhenius equation is applied to study the proton transfer mechanism. By calculating the Arrhenius plot, one can calculate the activation energy required to transmit the proton. The data of proton conductivity versus temperature is schematized for understanding the mechanism of conduction through the following Arrhenius equation (5):

$$\ln(\sigma T) = \ln \sigma_0 - \frac{E_a}{RT}$$
(5)

where σ and σ_0 stand for the protonic conductivity of the membrane (S/cm) and the preexponential factor (S/K cm), respectively; E_a shows the activation energy (kJ/mol); R displays the ideal gas constant (J/mol K); and T denotes temperature (K).

2.5.4. Oxidative stability

Fenton's reagent (3% H_2O_2 and 4 ppm FeSO₄) was used to investigate the oxidative stability of the membranes at 80 °C. A part of the membranes was cut and soaked in Fenton's reagent. Weight changes in the membranes were detected through the degradation time.

2.5.5. Fuel cell tests

Membrane Electrode Assemblies (MEAs) are made through a coated catalyst with the electrode method (CCE). Preparation of Pt-C (20 wt.% Pt)/PBI (as the binder and ionomer)/LiCl (as a stabilizer)/DMAc (3.6/1/0.2/38 by wt.) (as a catalyst solution) was conducted within 1 hour of ultrasonic disturbing. After painting the catalyst ink onto carbon cloth (Pt loadings: 0.5 mg/cm²), the catalyst loading in a contractual oven was calculated by drying it at 190 °C. The acid-doped membrane between the two parts of the gas-diffusing electrodes was sandwiched on each side and then heated under the pressure of nearly 50 kg/cm² at 130 °C for 5 min. was using A fuel cell testing system (FCT 1505, CHINO Inc., Japan) was employed to test the single cell performance at a 5% RH and 100, 150, and 180 °C under a dry condition. The single-cell of i-V was measured after it was activated at the constant current density of 600 mA/cm² for 8 h.

3. RESULTS AND DISCUSSION

3.1. Sulfonation of SPEES

Several factors affect the quality of the sulfonation reaction. The temperature and reaction time are factors determining the degree of polymer sulfonation. Control of these factors is desirable to obtain a polymer with optimum DS; therefore, concerning these factors and their control at the specified level, the SPEES polymer was synthesized with the required DS (Table 1). The membranes of high proton conductivity were used in the PEM fuel cells to produce

better fuel cell performance. The proton conductivity of PEES polymer was enhanced via PEES sulfonation. Proton conductivity and chemical stability are the two main parameters in the PEMs fuel cell. This indicates the strong effects of the two parameters on the membrane performance in the fuel cells so they must be optimized based on these two properties. The chemical stability and proton conductivity change for the SPEES polymer with varying DS. The highest level of proton conductivity is reached for the SPEES membranes within the DS range of 60-80% (Table 1). The chemical and mechanical stabilities of the membranes are reduced with the high-water adsorption induced by high sulfonation. The elevated DS led to augmented proton conductivity for the SPEES membranes. Nevertheless, a significant decrease occurred in the chemical stability of the mentioned membranes at high DS levels (more than 68%) and thus, the optimal DS of 68% was chosen for the SPEES membranes [35].

Membrane	Sulfonation time (h) at 10 °C	Proton conductivity (mS/cm) at 95% RH and at 25 °C
SPEES35	1.5	10
SPEES55	2.5	18
SPEES60	3.5	19
SPEES68	4	20
SPEES80	5	20

Table 1. Specification of SPEESx polymers

3.2. ATR spectra

Figure 1 shows ATR spectra of SPEESx membranes that confirm the incorporation of $-SO_3H$ groups to SPEES. The Absorption peak at 3385 cm⁻¹ is related to the O–H stretch of $-SO_3H$ group, which increased with increasing DS and absorbed moisture. The S–O, S=O, and O=S=O stretches were seen at 735, 1023, and 1078 cm⁻¹, respectively [10,43].

Figure 2 shows ATR spectra of PBISx-68 blend membranes. Several N–H stretching bands in the region of 3600–3000 cm⁻¹ are seen in PBI spectra. The elf-associated stretching of N–H and N–H stretching of free non-hydrogen bonds s have resulted in the peaks at 3195 and 3420 cm⁻¹, respectively. The aromatic groups of C–H have led to a peak of the stretching frequency at 3063 cm⁻¹. It is seen that with increasing SPEES/PBI weight ratio in the PBISx-68 blend membranes, a change towards a lower wide frequency at the peak of 3408 cm⁻¹ is obtained. The specific interaction of the N–H groups of PBI with SPEES functionalities has been displayed by the redshift indicated through the free N–H band of the blend membranes.



Figure 1. ATR spectra of SPEESx membranes

From the ATR spectra, it is obvious the interaction between N-H groups of PBI and -SO₃H groups of SPEES in the form of hydrogen bonding ensures the miscibility of the PBI-BSX blend membranes. In the previous works, the interactions of hydrogen bonds between the polymers in the blend membranes were corroborated by ATR spectra information [37,42,44].



Figure 2. ATR spectra of APBIS_{x-68} blend membranes

3.3. PAdop and proton conductivity

PBI proton conductivity based membrane is a function of the amount of PA doping level [6]. Studies show that PA has high thermal stability associated with low vapor pressure and the ability to direct proton at high temperatures [10]. PA generates a dynamic hydrogen-bonding network that can be propagated by simultaneously forming and breaking down hydrogen bonds

along the network. Its easy performance is due to the presence of a nitrogen atom (-N=) serving as a proton acceptor in the PBI molecule structure. The membrane's increased proton conductivity is triggered by the important role of free PA. Therefore, the membrane's performance, efficiency, and proton conductivity in the fuel cell are influenced by any factors affecting acid uptake, helping to maintain particularly at high temperatures. According to the studies, enhanced PA amount in the membrane is caused by the membrane's PA_{dop} content of greater than 3 mol [45].

Figure 3 displays the PA_{dop} plots of the APBIS_{x-y} blend membranes. The APBIS_{x-y} blend membrane exhibited high PA_{dop} than pure APBI membranes. The PA_{dop} of APBIS_{x-y} blend membranes increases with increasing DS of SPEES up 68%. The APBIS_{x-68} blend membranes demonstrated high PA_{dop} compared with APBIS_{x-50} and APBIS_{x-60} blend membranes. With increasing DS of SPEES, the PA_{dop} of APBIS_{x-y} blend membranes increases due to the increase of –SO₃H groups and the increased ionic interactions between PBI and SPEES. In APBIS_{x-y} blend membranes, PA_{dop} increases with increasing the weight ratio of SPEES/PBI up 15 wt.%. But in a high weight ratio of SPEES/PBI (greater than 15 wt.%), the PA_{dop} decreased. This result is due to the phase separation between SPEES and PBI and reducing effective interactions between PBI and SPEES and so decreasing the available active surface available for absorption of PA.



Figure 3. PA_{dop} plots of APBIS_{x-y} blend membranes

The plots of proton conductivity for the APBIS_{x-y} blend membranes, which show to be higher than those of pure APBI membranes, are portrayed in Figure 4. The main reason for this result is a strong interaction between PA, $-SO_3H$ groups of SPEES, and -NH groups of PBI in APBIS_{x-y} blend membranes. The H⁺ ions in the $-SO_3H$ groups of SPEES are responsible for proton transport in the APBIS_{x-y} blend membranes. Adding the SPEES with 68% of DS in APBIS_{x-y} blend membranes increases the size and connectivity of the ionic cluster of ionic channels in blend membranes. Hence, APBIS_{x-68} blend membranes showed to have high proton conductivity in comparison with APBIS_{x-50} and APBIS_{x-60} blend membranes. The reduced proton conductivity of APBIS_{x-y} blend membranes is due to phase separation in a high weight ratio of SPEES/PBI (more than 15 wt.%). The APBIS₁₅₋₆₈ blend membranes displayed the highest PA_{dop} (12 moles) and proton conductivity (40 mS/cm) as compared to the other APBIS_{x-y} blend membranes.



Figure 4. Proton conductivity plots of APBIS_{x-y} blend membranes

Figure 5 shows Arrhenius plots of the APBI and APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ membranes in the thermal range of 25–160 °C. The proton conductivities of APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ blend membranes are augmented by elevating temperatures. The charged species mobility enhanced with increasing temperature and the proton conductivity of the blend membranes was consequently improved.

Grotthuss mechanism and Vehicle mechanism are two main mechanisms that help proton transfer in APBI-based membranes. In the Vehicle mechanism, the membrane initially absorbs the proton, then it is released into the membrane, and on the other side it is repelled and the proton is removed from the membrane. In this case, due to the much smaller proton size compared to that of a hydrogen molecule, it can move under the influence of electric force in a suitable substrate. It is commonly used in membranes filled with water.

In dry environments or when the moisture content is very low, the Grotthuss mechanism mainly governs proton conduction. In these membranes, protons are often exchanged by agent groups (M) instead of by water molecules. The process of proton exchange in the mechanism of mutation is that the proton generates and breaks the hydrogen bond from one (M-H₃O⁺) to another (M-H₃O⁺) and passes through the membrane. The APBIS₁₅₋₆₈ membranes showed 101 mS/cm proton conductivity at 160 °C which was high compared with previously prepared blend

membranes. The activation energy (E_a) is referred to as the minimum energy needed for proton conduction.



Figure 5. Arrhenius plots of the APBI, APBIS₁₀₋₆₈, and APBIS₁₅₋₆₈ membranes

Its explored values would lead to the predictable key mechanism of proton transport in PEMs. $ln(\sigma)$ versus 1000/T (K) representing the slope of Arrhenius plots contribute to the extraction of the proton transport activation energies (E_a) of 31 and 19 kJ.mol⁻¹ in the APBIS₁₀₋₆₈ and APBIS15-68 bled membranes, respectively. The predominant Grotthus mechanism of the membrane's proton transport was exhibited by the outcomes. This predominance is confirmed by the amount of activation energy range of 14–40 kJ.mol⁻¹ [16]. At high temperatures, The Grotthuss mechanism helps proton transport in the APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ bled membranes as they are transferred between the lattice and 'hopping' ions carrying charges throughout the proton transfer network.

Generally, the proton transfer in the APBI based high-temperature PEMs manages with the Grotthuss mechanism by hopping the proton between PA and ion pairs of $H_4PO_4^+/H_2PO_4^-$. The pure liquid PA has the highest basic proton conductivity. Some researchers reported that the proton conductivity via vehicular mechanism is just for approximately 2.6% of the whole conductivity of PA-PBI-based high-temperature PEMs. They described the Grotthus mechanism as the key mechanism for proton conduction with a transference number of t~H⁺ 97.5% for PA. The concentration of PA can affect the proton transfers in the Grotthus hopping mechanisms.

3.4. Morphological studies

Varied factors, including size, morphology, ionic channel connectivity, and distribution, of membranes closely determine PEM proton conductivity [43]. Proton conductivity changes may

be caused by changes in morphology [16,46]. SEM analysis was applied to study the blend membrane morphology. Figure 6 shows SEM cross-section images for the PBIS₁₀₋₆₈, PBIS₁₅₋₆₈, PBIS₂₀₋₆₈, and PBIS₂₅₋₆₈ blend membranes. The uniform distribution of SPEES68 polymer in the PBI matrix is seen in the blend membrane of PBI-BS₁₅ in Fig. 6(b), while an integral membrane surface with no defects or cavities is achieved, thus confirming the excellent compatibility between PBI and SPEES in the PBIS₁₅₋₆₈ blends membranes. This indicates that the interaction of the -NH groups of PBI with -SO₃H groups of SPEES based on hydrogen bonding has a great effect on the uniform morphology of PBIS₁₅₋₆₈ blend membranes. The phase separation occurs by increasing the weight ratio of SPEES/PBI in PBIS₂₀₋₆₈ (Fig. 6(c)) and PBIS₂₅₋₆₈ (Fig. 6(d)) blends membranes. The uniform or non-uniform distribution of polymers in blend membranes can affect the properties of the membranes, including mechanical stability, proton conductivity, and acid uptake [43,47].



Figure 6. Cross section SEM images of the $PBIS_{10-68}$ (a), $PBIS_{15-68}$ (b), $PBIS_{20-68}$ (c), $PBIS_{25-68}$ (d) membranes

Figure 7 shows AFM phase images of PBIS₁₅₋₆₈, PBIS₂₀₋₆₈, and PBIS₂₅₋₆₈ blend membranes. Figure 7(a) shows the PBIS₁₅₋₆₈ blend membrane has a homogeneous surface without clear phase separation. These results are indicative of the efficient SPEES68 interactions in the PBI matrix and its uniform distribution in the PBIS₁₅₋₆₈ blend membrane. The phase separation was observed in PBIS₂₀₋₆₈ and PBIS₂₅₋₆₈ blend membranes (Figures 7(b) and 7(c)). In AFM phase images of the membranes, bright and dark areas are respectively related to hydrophilic (–SO₃H groups) and hydrophobic regions. The different properties of membrane transfer are greatly affected by the size and binding states of the hydrophilic regions, which depend on the SPEES/PBI weight ratio in the PBIS_{x-68} blend membrane. The roughness average of membrane surfaces can be obtained from AFM 3D images. When the SPEES68 polymer is added to the PBI matrix, the surface roughness of $PBIS_{x-68}$ blend membranes affects the mobility of the polymer chain and proton transfer.



Figure 7. AFM phase images of the PBIS₁₅₋₆₈ (a), PBIS₂₀₋₆₈ (b), and PBIS₂₅₋₆₈ (c) membranes

Figure 8 displays 3D AFM surface images of PBIS₁₅₋₆₈, PBIS₂₀₋₆₈, and PBIS₂₅₋₆₈ blend membranes. The PBIS₁₅₋₆₈ blend membranes demonstrated uniform roughness (Figure 8(a)). The uniform roughness of the PBIS₁₅₋₆₈ blend membranes can lead to better PA molecule adsorption and membrane proton conductivity due to the high surface level.



Figure 8. 3D AFM surface images of $PBIS_{15-68}$ (a), $PBIS_{20-68}$ (b), and $PBIS_{25-68}$ (c) blend membranes

Since the PBI and SPEES in the $PBIS_{x-68}$ blend membranes are compatible, an enhanced contact surface between the membrane and electrodes in the MEA can be also resulted from the uniform roughness of the membrane.

3.5. Thermal stability

Figure 9 shows TGA plots of APBI, SPEES68, PBIS₁₀₋₆₈, and PBIS₁₅₋₆₈ membranes. As shown in Figure 9, PBI polymerization occurs at around 600 °C and polymerization of the SPEES polymer is about 500 °C. There are three weight loss stages in the TGA plots of the blend membranes. The first weight loss, which occurs at a temperature of below 100 °C, is triggered by the physical (weak) and chemical (strong) bond losses between water molecules. The second weight loss happens within a range of 224-370 °C, which is caused by the -SO₃H group elimination from the polymer. At temperatures below this temperature range, -SO₃H groups, which do not create hydrogen bonds with adjacent chains, and so-called free ones, are separated from the polymer chains, and at temperatures above this range -SO₃H groups which are in the membrane, are destroyed. The final weight reduction starts at nearly 540 °C, which is related to the destruction of the membrane's main chain. The PBIS₁₀₋₆₈ and PBIS₁₅₋₆₈ blend membranes demonstrated high thermal stability in a temperature range of 200-300 °C in comparison with pure PBI membranes. This finding confirms that the blend membranes contain adequate thermal characteristics for the HT-PEM fuel cells (up to 300 °C).



Figure 9. TGA plots of APBI, SPEES68, PBIS₁₀₋₆₈ and PBIS₁₅₋₆₈ membranes

The miscibility of blend membranes can be determined by measuring their glass transition temperature (T_g). DSC studies prove specific interactions between the SPEES and PBI membranes in the blend membrane that causes the membrane to become miscible. The miscible blend membranes only show one T_g . When the two polymers form a completely immiscible or semi-miscible blend membrane, they show more than one value for Tg since having more than

one phase, while each phase has one T_g at a given temperature. The T_g of PBI, SPEES is 345 and 192 °C, respectively. The T_g of the PBIS₁₅₋₆₈ and PBIS₂₀₋₆₈ blend membranes was measured using DSC. The DSC graph in Figure 10 displays that the PBIS₁₀₋₆₈ and PBIS₁₅₋₆₈ blend membranes only show a one T_g . The T_g of the blend membrane is between the T_g of the pure PBI and SPEES, which can confirm the compatibility of the PBI and SPEES, and also indicate the polymer chain mobility is not inhibited by the ionic interactions. The PBIS₁₀₋₆₈ and PBIS₁₅₋₆₈ blend membranes. Lowering the T_g value of the blend membranes increases their flexibility, and so increased flexibility increases the membrane mobility and proton conductivity [26, 47].



Figure 10. DSC plots of the PBIS₁₀₋₆₈ and PBIS₁₅₋₆₈ blend membranes

3.6. Mechanical and chemical stability

Figure 11 depicts the mechanical properties of the APBIS_{x-68} blend membranes. The APBIS_{x-68} blend membranes showed a high elongation compared with pure APBI membrane. When the SPEES polymer introduces in the APBIS_{x-68} blend membranes structure, the molecular cohesion in the PBI membrane matrix decreases and so the polymer flexibility increases. SPEES plays a plasticizing role, thus enhancing elongation when the APBIS_{x-68} blend membranes are broken. The APBIS_{x-68} blend membranes revealed high tensile strength compared to the pure APBI membrane. This could be ascribed to the strenuous hydrogen bonding of the -SO₃H group with the PBI nitrogen atom. The APBIS_{x-68} blend membrane's tensile strength decreases in the high weight ratio of SPEES/PBI (more than 15 wt.%) due to the phase separation which was confirmed by AFM analysis. Fenton reagent behavior at 80 °C was observed to examine the chemical stabilities of the PBI, PBIS₁₅₋₆₈, and PBIS₂₀₋₆₈ blend membranes compared to the PBI membrane due to the SPEES membrane's hydrophilic nature and low chemical stability. The increased SPEES amount was resulted from the decreased chemical stability of the PBIS₂₀₋₆₈ blend membrane; however, this

reduction was less for the chemical stability of PBIS₁₅₋₆₈ blend membranes at low SPEES amounts.



Figure 11. Mechanical stability plots of the APBIS_{x-68} blend membranes

The reason can be attributed to the acid-base interaction. Therefore, the interaction of SO_3H groups with PBI prevents the effects of hydroxyl and hydroperoxy radicals (•OH or •OOH) as Fenton's reagent products [48, 49]. In the PBIS₂₀₋₆₈ blend membrane, chemical stability decreases due to decrease interaction between the PBI and SPEES polymer.



Figure 12. Chemical stability plots of PBI, PBIS₁₅₋₆₈ and PBIS₂₀₋₆₈ membranes

X-ray diffraction analysis provides a qualitative evaluation of the amorphous or crystalline properties of membranes. In general, when the chains of the polymer are arranged regularly, the nature of the crystal increases. Considering the presence of van der Waals force between polymer chains and hydrogen bonds, irregular arrangement of polymers indicates their amorphous nature. Fig. 13 exhibits X-Ray patterns of diffraction for the PBI, PBIS₁₅₋₆₈, and PBIS₂₀₋₆₈ membranes. The PBIS₁₅₋₆₈ and PBIS₂₀₋₆₈ blend membranes exhibit lower crystallinity compared to the pure PBI. These results confirm the intermolecular hydrogen interaction

between PBI and SPEES destroying PBI's main molecular orientation. Lower crystallinity is indicative of more amorphous blend membranes. This means that the blend membranes show better flexibility according to the analysis results in mechanical strength, DSC and X-ray diffraction can be concluded that adding SPEES to PBI partially reduced brittleness and hardness of PBI and enhances its flexibility is somewhat reduced.



Figure 13. X-Ray diffraction patterns of PBI, PBIS₁₅₋₆₈ and PBIS₂₀₋₆₈ membranes

3.7. Fuel cell performance

MEA was made by the APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ blend membranes. The performance of the PEM fuel cell is expected to be ameliorated by elevating temperatures. For operating at high temperatures, the membranes fundamentally require optimum performance of fuel cells. Figure 14 portrays the polarization curves of APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ blend membranes at 160 °C and 180 °C. As shown in Figure 14, the APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ blend membranes show an excellent fuel cell performance compared with APBI membranes, especially at 180 °C. The APBIS₁₅₋₆₈ blend membranes due to the high proton conductivity demonstrate high fuel cell performance compared with APBIS₁₀₋₆₈ blend membranes. With increasing operating temperature, fuel cell performance based on APBIS₁₅₋₆₈ compared to APBI blend membranes is significantly enhanced. This performance improvement relates logically to the increased proton conductivity and improved kinetics of MEA's electrochemical reactions based on APBIS₁₅₋₆₈ blend membranes, as well as the reduction in the membrane matrix resistance against the proton transfer with increasing temperature. The current densities of 0.91 A/cm^2 at 0.45 V at 160 °C obtained for APBIS₁₅₋₆₈ blend membranes. As the APBIS₁₅₋₆₈ blend membrane-based PEM fuel cells undergo a higher power density (0.65 W/cm²) at 180 °C, a shift in current density towards a higher current (1.31 A/cm²) occurs. The fuel cell performance is enhanced by alleviating the contact resistance of the joint surface of the APBIS₁₅₋₆₈ blend membrane-based MEA. Compared to Celtic-P1000 acting as a commercial MEA at 180 °C, the APBIS₁₅₋₆₈ blend membranes showed power density development. The experimental results

were suggestive of the suitability of the $APBIS_{15-68}$ blend membranes in PEM high-temperatured fuel cell applications.



Figure 14. Polarization curves of APBIS₁₀₋₆₈ and APBIS₁₅₋₆₈ blend membranes at (a) 160 °C and (b) 180 °C with 0.5 mg/cm² Pt loading. The H₂ and O₂ were supplied to the anode and the cathode at flow rates of 300 ml/min and 500 ml/min respectively.

4. CONCLUSION

This study advanced miscible blends of PBI and SPEES by using the solution casting method. methods. The SPEES/PBI weight ratio and DS of SPEES in the prepared blend membranes were investigated as two important parameters. ATR analysis displayed the presence of a particular interaction between the PBI and SPEES in the miscible blend membranes, which represented more appropriate fuel cell performance induced by higher proton conductivity as compared to pure PBI membranes. The SPEES polymer was uniformly dispersed in the PBI matrix with an integrated membrane surface of no cavity or breakage . The blend membranes demonstrated high mechanical and thermal stabilities. The blend membrane potential for being utilized as high-temperatured PEM in fuel cell applications was corroborated by their high proton conductivity manifested by the high current density (1.30 A/cm^2 at 0.5 V) of SPEES/PBI at 180 °C.

Acknowledgments

The authors are grateful to Renewable Energy Research Center (Amirkabir University of Technology, Tehran, Iran) for the financial support of this work.

REFERENCES

- [1] M.B. Karimi, F. Mohammadi, and K.H. Hooshyari, J. Membr. Sci. 611 (2020) 118217.
- [2] M.B. Karimi, F. Mohammadi, and K.H. Hooshyari, J. Membr. Sci. 605 (2020) 118116.
- [3] K.H. Hooshyari, H. Rezania, V. Vatanpour, P. Salarizadeh, M.B. Askari, H. Beydaghi, and M. Enhesari, J. Membr. Sci. 612 (2020) 118436.

- [4] K.H. Hooshyari, M. Moradi, and P. Salarizadeh, Int. J. Energy Res. 44 (2020) 2617.
- [5] K.H. Hooshyari, S.N. Khanamiri, P. Salarizadeh, and H. Beydaghi, J. Electrochem. Soc. 166 (2019) F976.
- [6] M. Javanbakht, K.H. Hooshyari, M. Enhessari, and H. Beydaghi, Iranian Journal of Hydrogen & Fuel Cell 2 (2014) 105.
- [7] K.H. Hooshyari, M. Javanbakht, P. Salarizadeh, and A. Bageri, J. Iran Chem. Soc. 16 (2019) 1617.
- [8] A. Shabanikia, M. Javanbakht, H.S. Amoli, K.H. Hooshyari, and M. Enhessari, Electrochim. Acta 154 (2015) 370.
- [9] A.M. Attaran, A. Javanbakht, K.H. Hooshyari, and M. Enhessari, Solid State Ionics 269 (2015) 98.
- [10] K.H. Hooshyari, M. Javanbakht, L. Naji, and M. Enhessari, J. Membr. Sci. 454 (2014) 74.
- [11] H. Tang, S. Peikang, S.P. Jiang, F. Wang, and M. Pan, J. Power Sources 170 (2007) 85.
- [12] V. Neburchilov, J. Martin, H. Wang, and J. Zhang, J. Power Sources 169 (2007) 221.
- [13] K.H. Hooshyari, M. Javanbakht, A. Shabanikia, and M. Enhessari, J. Power Sources 276 (2015) 62.
- [14] A. Shabanikia, M. Javanbakht, H.S. Amoli, K.H. Hooshyari, and M. Enhessari, J. Electrochem. Soc. 161 (2014) 1403.
- [15] A. Shabanikia, M. Javanbakht, H.S. Amoli, K.H. Hooshyari, and M. Enhessari, Ionics 21 (2015) 2227.
- [16] A. Moheb, M. Javanbakht, and K.H. Hooshyari, Int. J. Hydrog. Energy 41 (2016) 2896.
- [17] K.H. Hooshyari, M. Javanbakht, and M. Adibi, Electrochim. Acta 142 (2016) 142.
- [18] K.H. Hooshyari, M. Javanbakht, and M. Adibi, Int. J. Hydrog. Energy 41 (2016) 10870.
- [19] D.C. Seel, and B.C. Benicewicz, J. Membr. Sci. 405 (2012) 57.
- [20] A. Chandan, M. Hattenberger, A. El-kharouf, S. Du, A. Dhir, V. Self, B. G. Pollet, A. Ingram, and W. Bujalski, J. Power Sources 231 (2013) 264.
- [21] M.A. Haque, A.B. Sulong, K.S. Loh, E.H. Majlan, T. Husaini, and R.E. Rosli, Int. J. Hydrogen Energy 42 (2017) 9156.
- [22] S. Bose, T. Kuila, T. Xuan, H. Nguyen, and N. Hoon, Prog. Polym. Sci. 36 (2011) 813.
- [23] S. Unugur Çelik, A. Bozkurt, and S.S. Hosseini, Prog. Polym. Sci. 37 (2012) 1265.
- [24] P. Salarizadeh, M. Javanbakht, S. Pourmahdian, M. Sabooni, and K. Hooshyari, Int. J. Hydrog. Energy 44 (2019) 3099.
- [25] P. Salarizadeh, A. Bagheri, H. Beydaghi, and K. Hooshyari, Int. J. Energy Res. 43 (2019) 4840.
- [26] P. Go, J.A. Asensio, E.M. Sa, and J.A. Asensio, A Chemical Quest. Chem. Soc. Rev. 39 (2010) 3210.
- [27] Q. Li, J. Oluf, R.F. Savinell, and N.J. Bjerrum, Progress Polymer Sci. 34 (2009) 449.

- [28] M. Hazarika, and T. Jana, ACS Appl. Mater. Interfaces 10 (2012) 5256.
- [29] M. Won, So. Kwon, and T. Kim, Industrial Eng. Chem. 29 (2015) 104.
- [30] D. Joseph, N. Krishnan, D. Henkensmeier, J. Hyun, J. Sun, H. Choi, H. Kim, J. Han, and S.W. Nam, J. Mater. Chem. A 5 (2017) 409.
- [31] G.A. Giffin, S. Galbiati, M. Walter, K. Aniol, C. Ellwein, J. Kerres, and R. Zeis, J. Membr. Sci. 535 (2017) 121.
- [32] R.E. Rosli, A.B. Sulong, W.R.W. Daud, M.A. Zulkifley, T. Husaini, M.I. Rosli, E.H. Majlan, M.A. Haque, Int. J. Hydrogen Energy 42 (2017) 9293.
- [33] L. Wang, Z. Liua, J. Ni, M. Xu, C. Pan, D. Wang, D. Liua, and L. Wang, J. Membrane Sci. 572 (2019) 350.
- [34] R. Akay, K. Ata, T. Kadıoglu, and C.C. Elik, Int. J. Hydrogen 43 (2018) 18702.
- [35] Z. Taherkhani, M. Abdollahi, and A. Sharif, Solid State Ionics 337 (2019) 122.
- [36] V. Deimede, G. Voyiatzis, J. K. Kallitsis, L. Qingfeng, and N. J. Bjerrum, Macromolecules 20 (2000) 7609.
- [37] E. Erdal, T. Erdogan, and S.C. Serdar, Int. J. Hydrogen Energy 35 (2010) 3736.
- [38] S. Neelakandan, P. Kanagaraj, R.M. Sabarathinam, A. Muthumeenal, and A. Nagendran, J. Solid State Electrochem. 19 (2015) 1755.
- [39] K.H. Hooshyari, S. Heydari, M. Javanbakht, H. Beydaghi, and M. Enhessari, RSC Advances 10 (2020) 2709.
- [40] P. Hosseinabadi, K.H. Hooshyari, M. Javanbakht, and M. Enhessari, New J. Chem. 43 (2019) 16232.
- [41] H. Beydaghi, M. Javanbakht, A. Bagheri, H. Ghafarian-Zahmatkesh, and K.H. Hooshyari, Iranian J. Hydrogen Fuel Cell 4 (2017) 1.
- [42] V. Kumar, S. Mondal, A. Nandy, and P.P. Kundu, Eng. J. 111 (2016) 34.
- [43] R. Guan, H. Dai, C. Li, J. Liu, and J. Xu, J. Memb. Sci. 277 (2006) 148.
- [44] S. Kaliaguine, S. D. Mikhailenko, K. P. Wang, P. Xing, G. Robertson, and M. Guiver, Catal. Today 82 (2003) 213.
- [45] S. Neelakandan, P. Kanagaraj, R. M. Sabarathinam, and A. Nagendran, Appl. Surf. Sci. 359 (2015) 272.
- [46] P. Salarizadeh, M. Javanbakht, S. Pourmahdian, and H. Beydaghi, Chem. Eng. J. 299 (2016) 320.
- [47] P. Maheswari, P. Barghava, and D. Mohan, D. J. Polym. Res. 20 (2013) 74.
- [48] S.M.J. Zaidi, Electrochim. Acta 50 (2005) 4771.
- [49] G. Qian, B.C. Benicewicz, and F. Sch, Inc. J. Polym. Sci. A (2017) 1831.

Copyright © 2023 by CEE (Center of Excellence in Electrochemistry)

ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY (<u>http://www.abechem.com</u>) Reproduction is permitted for noncommercial purposes.