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Blend Membranes of Highly Phosphonated Polysulfone and Polybenzimidazoles for High Temperature Proton Exchange Membrane Fuel Cells

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The aim of the presented work is to develop a polymer electrolyte having the specific composition of polysulfone (PSU) with phosphonic acid groups in the tethered form and polybenzimidazoles, doped with phosphoric acid, which facilitates self-ion transfer. The blended membranes show high proton conductivity (3.8×10^{-2} S/cm at 170°C at 25% RH) and have good thermal and mechanical properties.

Introduction

Proton conduction in polymer membranes in fuel cells is due to the vehicular, Grotthuss (hopping or structure diffusion), and segmented motion mechanisms. These mechanisms are dependent on the morphology of the polymers as well as the proton conducting functional groups.

It is observed that polymers containing acid groups mainly facilitate structure diffusion and vehicular transport mechanisms for proton transport. However, the presence of these acid groups imposes a limitation on the operating temperature ($<90^\circ\text{C}$) (1). For the vehicular proton transport mechanism, an aqueous media is essential to act as a mobile phase to facilitate the conduction of protons. Nevertheless, the presence of an aqueous media acts as a plasticizer and adversely affects the mechanical properties (swelling), increases the permeability of the fuel and oxidant, etc (2). On the other hand, the segmental proton transfer mechanism depends on the segmental motion of the polymer backbone, which requires a very low glass transition temperature that limits its mechanical properties, especially at high temperatures (3). In the Grotthuss mechanism, the proton, or protonic defects, diffuse through the hydrogen bond network by formation of cleavage of bonds and the proton is transferred through self or auto ionization (4). For example, at high temperatures in imidazole, protonic defects form and the proton is conducted through hydrogen bonding. Considering the limitations and advantages of all of the above three mechanisms, the transport phenomena involved, conformational, morphological contrast, mechanical strength, permeability of fuel/oxidant, and its temperature dependency etc., a polymer material needs to be designed and developed that can satisfy all the necessary properties and provide a robust material which can sustain the harsh oxidation/reduction environment.

In this study, we look at the use of highly phosphonated polysulfone (PSU) and PBI blend membranes to achieve the desired properties for use in high temperature PEM fuel cells.

Experimental

Materials And Methods

Bromomethylmethyl ether, tin (IV) bromide (SnBr_4), Triethyl phosphate, and Diethyl carbitol, were purchased from Aldrich Chem and used without purification. Polysulfone (Udel) (M.W.40000) obtained from Solvay Advanced Polymers, Dry solvents were purchased from Aldrich chem. where as other solvents were purchased from Honeywell (HPLC grade). ^1H NMR spectra were obtained on a Bruker NMR spectrometer operating at a proton frequency of 500 MHz. using (DMSO-d_6) and ($\text{CDCl}_3\text{-d}$) as solvents and the reference material 2.50 and 7.26 for DMSO-d_6 and CDCl_3 respectively for recording NMR spectra at room temperature. Thermogravimetric analyses (TGA) were recorded using Perkin Elmer TGA-7 instrument from 30 to 800 °C with a scanning rate of 10 °C min^{-1} in N_2 atmosphere.

Bromomethylation of polysulfone (DBMPSU)

100 mL Schlenk was loaded with polysulfone (2 g, 4.2 mmol) and dissolved in dry dichloroethane (24 mL). Bromomethylmethyl ether (1.84 mL, 22.2 mmole) was added to this solution and the reaction mixture was stirred at ambient temperature for 1 h. Then tin (IV) bromide (1.48 g, 3.31mmol) was added to this flask drop wise at ambient temperature and reaction mixture was heated at 60 °C under Argon. The progress of the reaction was monitored by ^1H NMR spectroscopy and after 6 days 200% degree of bromomethylation was obtained. The reaction mixture was precipitated in methanol (300 mL) and polymer was isolated by filtration. The polymer was purified by dissolution in dichloroethane and precipitation with methanol. Finally, the polymer was dried at 70 °C under vacuum for 12 h. $^1\text{HNMR}$ δ : 8.9 (4H), 7.35 (2H) 7.15 (2H), 7.1 (4H), 6.98 (2H), 4.46 (4H), 1.7 (6H).

Phosphonation of bromomethylated polysulfone

Dibromo methyl polysulfone (DBMPSU) (2 g) was loaded into a 100 mL round-bottom flask and dissolved in anhydrous NMP (30 mL). Diethyl carbitol (24 mL) and triethyl phosphate (12 mL) were added to the polymer solution. The reaction mixture was heated at 140 °C. Aliquots were taken after 2.5 h and 5 h and characterized by $^1\text{HNMR}$ spectroscopy, showed incomplete reaction. After 7.5 h reaction was stopped and cooled to room temperature. The polymer solution was precipitated in deionized water (300 mL) with vigorous stirring. Polymer was filtered and washed with water several times. Polymer was purified by dissolved in DMSO and precipitated in deionized water. Filtered the polymer, washed with water and dried in vaccum oven at 60 °C for 12 h. 2.2 g (92%) yield was obtained. $^1\text{HNMR}$ δ : 8.9 (4H), 7.35 (2H) 7.15 (2H), 7.1 (4H), 6.98 (2H), 4.46 (4H), 3.8 (8H), 3.15 (4H), 1.7 (6H), 1.05 (12H).

Hydrolysis of Phosphonic Acid Ester to Phosphonic Acid form (DPA-PSU)

Phosphonic Acid Ester form of polymer (1 g), 5N hydrochloric acid (30 mL) were taken into round-bottom flask and refluxed for 12 h. Then polymer was filtered and washed with several times with water and dried in vacuum oven for 12 h at 60 °C. 90% yield was obtained. ¹HNMR δ: 8.9 (4H), 7.35 (2H) 7.15 (2H), 7.1 (4H), 6.98 (2H), 4.46 (4H), 2.81 (4H), 1.7 (6H).

Synthesis of Polybenzimidazole (PBI)

A mixture of tetraamino benzidine (TAB), 0.5 g (0.00233 mol) and polyphosphoric acid (PPA), 15 g contained in a 50 mL three necked round bottom flask, equipped with a mechanical stirrer, nitrogen gas inlet was heated at 140 °C with stirring under a stream of nitrogen. isophthalic acid (IPA), 0.378 g (0.00233 mol) was added slowly with stirring to the solution and the temperature was raised to 170 °C in 2 h to give homogeneous solution. The solution was further heated to 200 °C and maintained at this temperature for 12 h under nitrogen purge.

The viscous solution was then poured into 200 mL water to precipitate the polymer. The polymer was filtered and washed repeatedly with water. To remove residual phosphoric acid, the polymer was stirred in 10% sodium bicarbonate solution overnight and washed with water to neutrality followed by repeated hot water wash to eliminate sodium bicarbonate, if any. Then polymer was washed with acetone to remove the water and finally polymer was dried at 100 °C for 24 h and 150 °C for another 24 h in vacuum oven. A brown color polymer was obtained. The yield of the polymer was about 97% (0.69 g).

DPPSU and PBI blend membrane Preparation

Polybenzimidazole (0.268 g) and phosphonated PSU in ester form (0.6 g) were dissolved in 15 mL and 25 mL dimethylacetamide (DMAc) respectively in conical flask. Solutions of PBI and phosphonated PSU in ester form in DMAc were mixed in 1:1 mole ratio and stirred for 2 h for complete mixing then filtered through G0 sintered funnel to get the clear solution and poured into clean Petri-dish. Petri-dish was placed oven at 85°C overnight. Good membrane was formed with even thickness.

Hydrolysis by HCl

Phosphonic Acid Ester form of PSU and PBI blend membrane was hydrolyzed by 5N. hydrochloric acid (70 mL) by refluxing for 5 days to get the phosphonic acid form of PSU and PBI cross-linked membrane. The obtained membrane is good and stable.

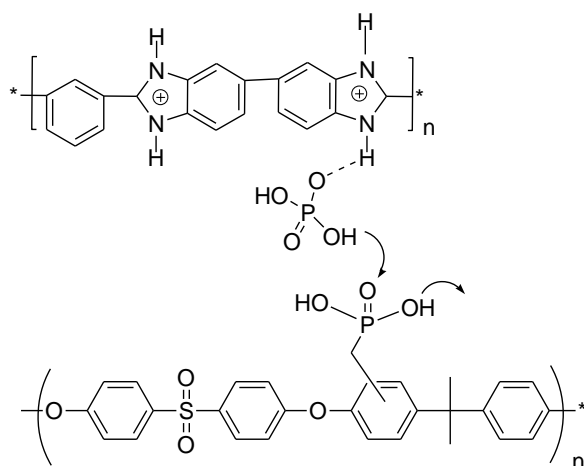


Figure 1. Possible mechanisms of DPPSU-PBI blend membranes

Acid Doping

To determine the H_3PO_4 uptake, the weighed samples membranes were immersed in the 85% of H_3PO_4 for 48 h at room temperature. The weight gain due to both water and phosphoric acid was obtained by weighing the sample, withdrawn from acid, again after wiping off adhered phosphoric acid from the sample with tissue paper. For determining the acid uptake by membranes, the doped membranes were dried at $100\text{ }^\circ\text{C}$ under vacuum until an unchanged weight was obtained. The acid uptake in wt % was determined by using the equation,

$$PU = \frac{(W_w - W_d)}{W_d}$$

Where W_d and W_w are the weight of dry and doped membrane samples respectively.

Water Sorption

Water sorption and desorption measurements were conducted using Dynamic Gravimetric Vapor Sorption (DVS) (DVS-Advantage, Surface Measurement Systems). The DVS system measures vapor uptake and loss gravimetrically using a microbalance with mass resolution of $\pm 0.1\text{ }\mu\text{g}$. The test procedure below is adapted from the method used by Burnett (5).

A small sample ($\sim 5\text{ mg}$) of the membrane was placed in a stainless steel mesh sample pan (400 holes/in) to allow for the vapor to flow directly to all surfaces of the sample. The sample pan was then placed in the DVS at $25\text{ }^\circ\text{C}$ and dried for 2 hr at 0% RH to establish the dry mass. After drying, the RH was stepped from 0% to 80% in 20% steps then to 90% and 95% and back to 0% along the same steps. Each step was held for 2 hr or until mass equilibrium was reached. Mass equilibrium was determined by the percentage change in mass with respect to time ($dm/dt = 0.005$).

Membrane Conductivity

Impedance measurements were conducted using Membrane Test System (MTS) (MTS 740, Scribner Associates, Inc.). The MTS is a through plane, AC impedance technique that allows for the control of sample temperature and relative humidity (RH). Impedance is measured using an SI 1260 impedance/gain-phase analyzer (Schlumberger Technologies, Inc.) and ZPlot software (Scribner Associates, Inc.) for four-terminal impedance spectroscopy. The electrode configuration is shown in Figure 2. Cell assembly and test procedure below adapted from the method used by Cooper (6, 7).

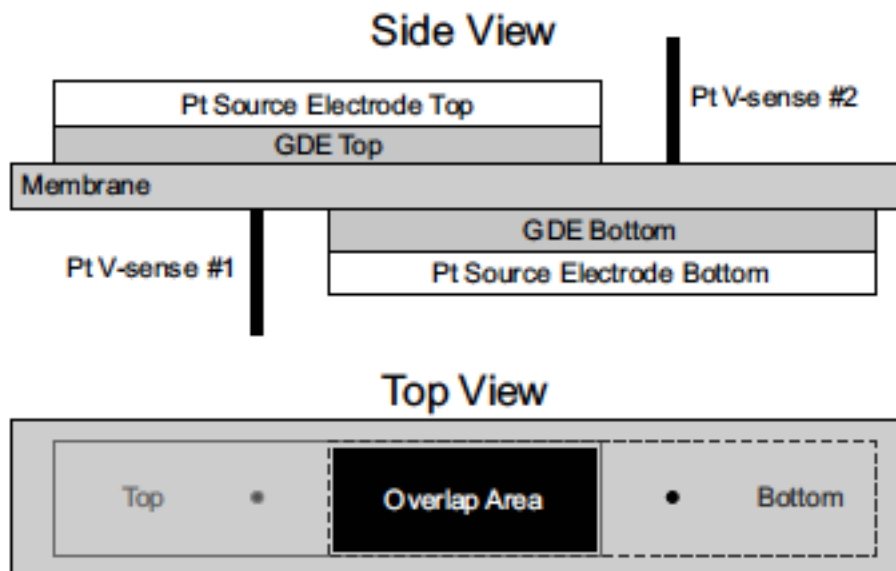


Figure 2. Illustration of the electrode/sample configuration (5)

Sample Prep and Cell Assembly: A sample is cut to 1.0cm X 3.0cm and the thickness measured. The sample is sandwiched between gas diffusion electrode (GDE) (IRD Fuel Cell Technology PEM GDE) materials that were attached to the platinum source electrodes using conductive carbon paint. The GDE allows for the flow of water vapor to and from the surface of the sample during testing. The sample is compressed between the electrodes with a loading of 2.151 ± 0.017 MPa (310 ± 2.5 psi) measured with a calibrated force spring and dial displacement indicator. The sample was then loaded into the environmental chamber that controls sample temperature (30°C to 180°C), dew point (30°C to 120°C), pressure (ambient to 230 kPa_a), and gas (N₂ or H₂).

Test Conditions: The samples were conditioned for 2 hr at 70% RH after which humidity was stepped in 10% intervals, 70% to 20% to 90% then to 95%, holding for 30 min at each RH step before measuring membrane resistance. This method was used at three temperature/pressure conditions (30°C and 80°C at 100 kPa_a and 120°C at 230 kPa_a). Samples were tested under nitrogen.

For testing above 120°C , the test method was modified to account for the 120°C dew point limit. Samples were conditioned at the maximum obtainable RH for 2 hr (40% at

150°C, 30% at 160°, and 25% at 170°C) after which humidity was stepped in 5% intervals, RH_{max} to 0% to RH_{max} , holding for 30 min at each RH step before measuring membrane resistance. Pressure for these temperatures was held at 280 kPa_a. Samples were tested under nitrogen.

Impedance Measurements: After holding the sample at a given RH for 30 min, impedance was measured using voltage controlled frequency sweep spectroscopy (10 mV_{AC} at 0 V_{DC}, 1 MHz to 1 Hz, 10 steps/decade).

Results and Discussion

We have synthesized phosphonic acid tethered polysulfone. In the first step, the higher degree (200%) of bromomethylation of polysulfone without cross-linking side reactions was achieved by a careful selection of reaction parameters such as time and temperature with quantitative yield. The incorporation of dibromomethylation group was confirmed by the appearance of a new singlet peak at δ 4.47 ppm in the 1H NMR spectrum. Obtaining higher degree of bromomethylation of PSU was one of the objectives of this work in order to obtain two phosphonic acid groups per repeat unit of PSU. Phosphonation of bromomethylated PSU was done at 140 °C by utilizing the Michaelis-Arbuzov reaction with diethyl carbitol to avoid the gelation. In the final step, phosphonate esters form of PSU was successfully hydrolysed to phosphonic acid form by using 5N HCl. Complete phosphonation of reaction was confirmed by 1H NMR spectroscopy. In the 1H NMR spectrum of the diphosphonated acid form of PSU in which two peaks of $-CH_2-CH_3$ of phosphonate esters at δ 1 ppm and δ 3.6 ppm respectively have completely disappeared and new peak of $-OH$ at δ 10.5 ppm has appeared.

Samples of DPPSU, DPPSU-PBI, and H_3PO_4 doped DPPSU-PBI were prepared and cast into membrane films for water sorption and conductivity testing (Figure 1). The cast membranes had thicknesses between 50 and 150 μm .

Thermal Properties

The thermal stability of these polymers was studied by thermo-gravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 10 °C min^{-1} . The thermograms are shown in Figure 3.

The thermal stability of the polymers was studied by TGA (Figure 3). An examination of thermal data reveals that the phosphonic acid has significant effect on thermal properties of polysulfone. The initial decomposition temperature of bromomethylated, phosphonic acid ester, phosphonic acid form polysulfone, Blend membrane of phosphonic acid ester and PBI, phosphoric acid doped blend membrane, PBI and polysulfone was 287°C, 305°C, 410°C, 430°C, 200°C and 465°C respectively. In the phosphonic acid form polysulfone, blend membrane of phosphonic acid ester PBI and phosphoric acid doped blend membrane the continuous weight loss was observed up to 400 °C which is attributed to the formation of anhydrides by the creation of P-O-P linkages of phosphonic acid and phosphoric acid (8). These anhydrides may be formed reversible desorption of water generated by the condensation of phosphonic acid (8).

However, main chain degradation of phosphonic acid form polysulfone was observed around 400 °C.

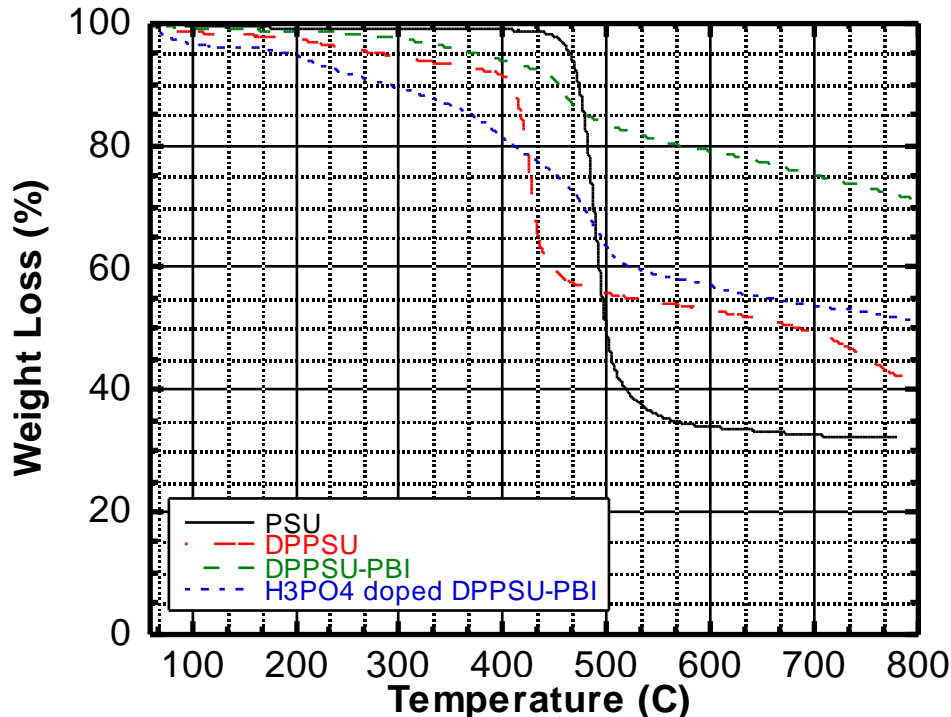


Figure 3 Thermograms of polymers in N₂ atmosphere (purging rate 20 mL/min) recorded at a heating rate 10 °C/min.

Doping Study

Polymer electrolyte membranes based on PBI are generally doped with phosphoric acid and the doping level of H₃PO₄ in PBI plays an important role in proton conductivity. The acid uptake capacity of blend membrane of phosphonic acid tethered polysulfone and PBI was determined by doping in 85% H₃PO₄ solutions for 48 h at room temperature. The doping level is defined as the weight percent of acid per gram of the polymer. It is well known that PBI is generally doped in the 85% H₃PO₄ at room temperature. After 48 h PBI take up ~300 wt% phosphoric acid. However 1:1 molar ratio of blend membrane of phosphonic acid tethered polysulfone and PBI take up 210 wt % H₃PO₄. As expected, the doping level of blend membrane decreases compared with pristine PBI. This may be due to the ionic bonding between phosphonic acid groups and PBI and decrease concentration of acid uptake groups.

Water Sorption

DVS experiments were performed on DPPSU, DPPSU-PBI, and H₃PO₄ doped DPPSU-PBI to determine membrane hydration time and total water sorption at 25°C. Figure 4 shows the water sorption/desorption curves obtained. It can be seen that the sample mass changes with the changes in RH. Each RH step was set to move on after 2 hr regardless of whether or not the equilibrium criterion ($dm/dt = 0.005$) was satisfied. While equilibrium was not reached by each sample at each RH step, the dm/dt values at the end of each step were <0.1.

From the sorption/desorption profiles, sample isotherms were calculated using the equilibrium state of each step. There is little change in water uptake between the DPPSU and DPPSU-PBI membranes, 16 wt% and 18 wt% respectively. However, there is a significant increase in water uptake after doping with phosphoric acid. The addition of the acid allows for the uptake of 105 wt% water (figure 5).

Membrane Conductivity

Conductivity of the membranes was conducted at a variety of environmental conditions. The DPPSU shows conductivity of order 10^{-2} S/cm with minimal dependence on RH (figure 6). Blending with PBI results in a significant decrease in conductivity and RH dependence. Conductivity increases by several orders of magnitude as humidity is increased from dry to 95%RH, however, the membrane does not recover the level of conductivity shown by the DPPSU membrane (figure 7).

Doping the DPPSU-PBI blend with phosphoric acid resulted in an increase in conductivity, returning to and exceeding the conductivity of the DPPSU membrane. The RH dependence was also significantly reduced. The first sample tested showed a significant reduction in conductivity at high temperature as compared to low temperature. A second sample was run starting at high temperature in an attempt to reveal effects of the test duration. The second sample showed significantly higher conductivity at high temperature than observed in the first sample, while showing reduced conductivity when returning to low temperatures (figure 8). The cause of this is likely to be the loss of the phosphoric acid during humidity and temperature cycling. While high conductivity was achieved at low humidity conditions, it is apparent from the DVS measurements that this polymer still contains a large weight percent of water at low humidity (7 wt% at 20%RH for H_3PO_4 doped DPPSU-PBI as compared to 2 wt% at 20%RH for DPPSU).

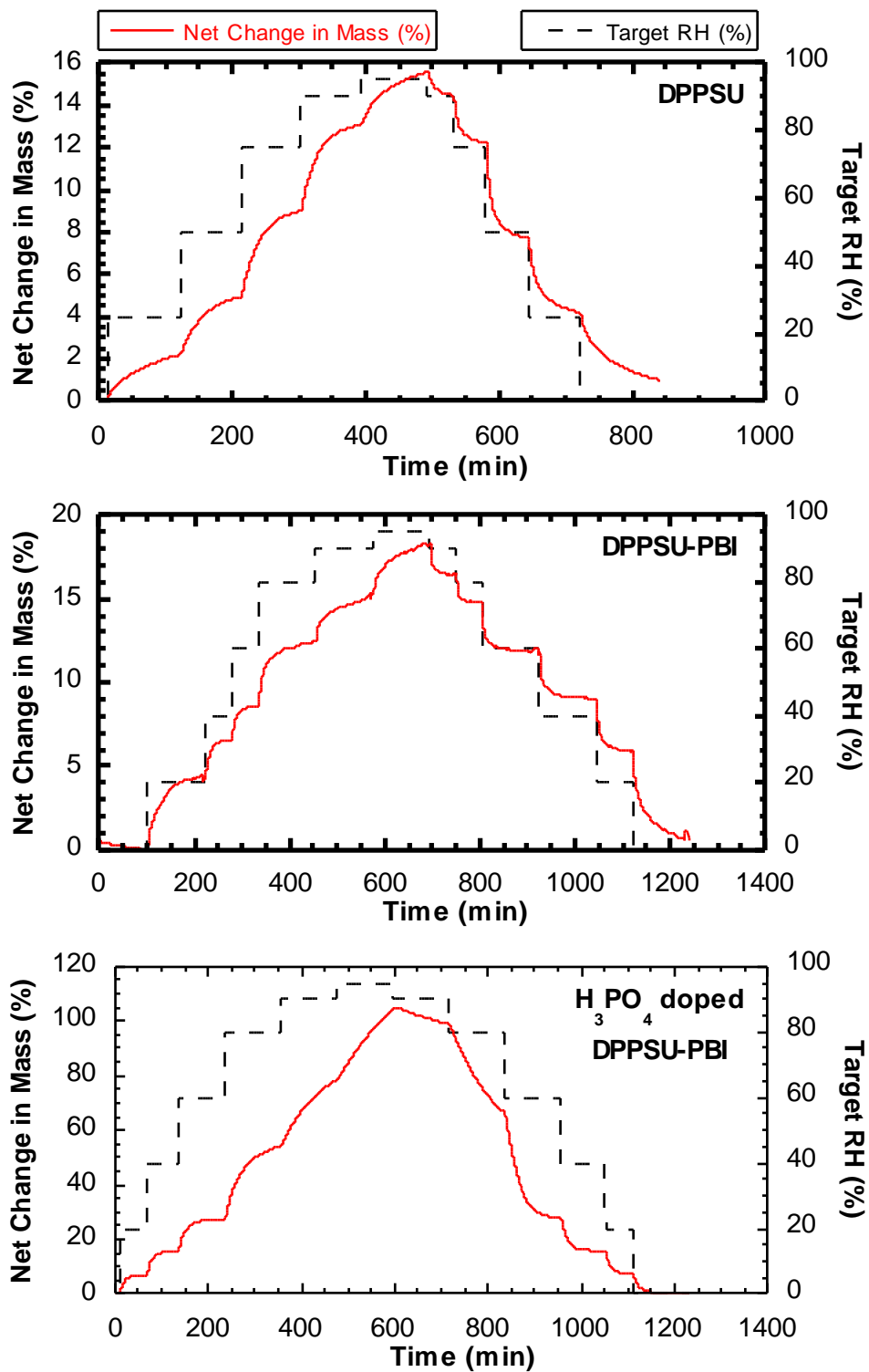


Figure 4. Water sorption/desorption profiles for DPPSU, DPPSU-PBI, and H₃PO₄ doped DPPSU-PBI at 25°C. The net mass change as a function of time is shown by the solid line (left axis) and the target RH is represented by the dashed line (right axis).

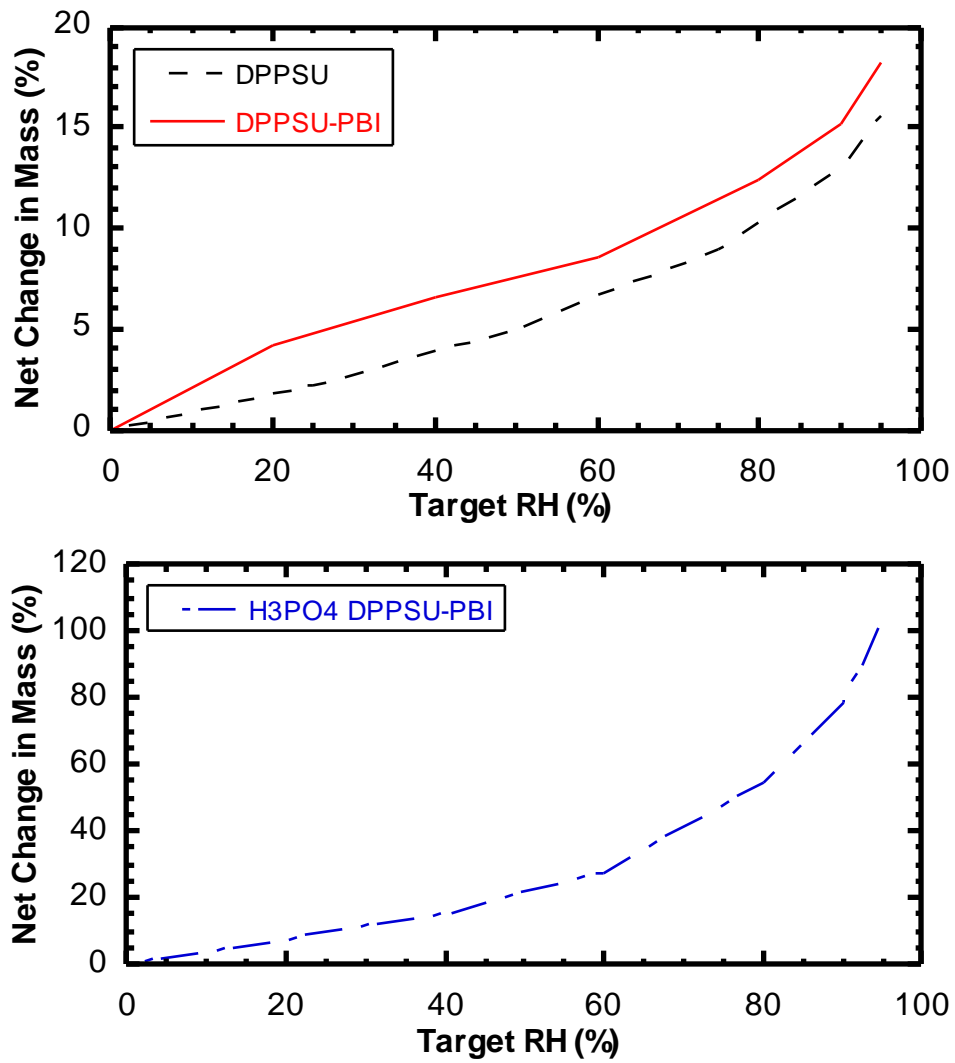


Figure 5. Water sorption isotherms of DPPSU, DPPSU-PBI, and H₃PO₄ doped DPPSU-PBI. Doping DPPSU-PBI with H₃PO₄ causes a significant increase in the amount of water taken up by the membrane.

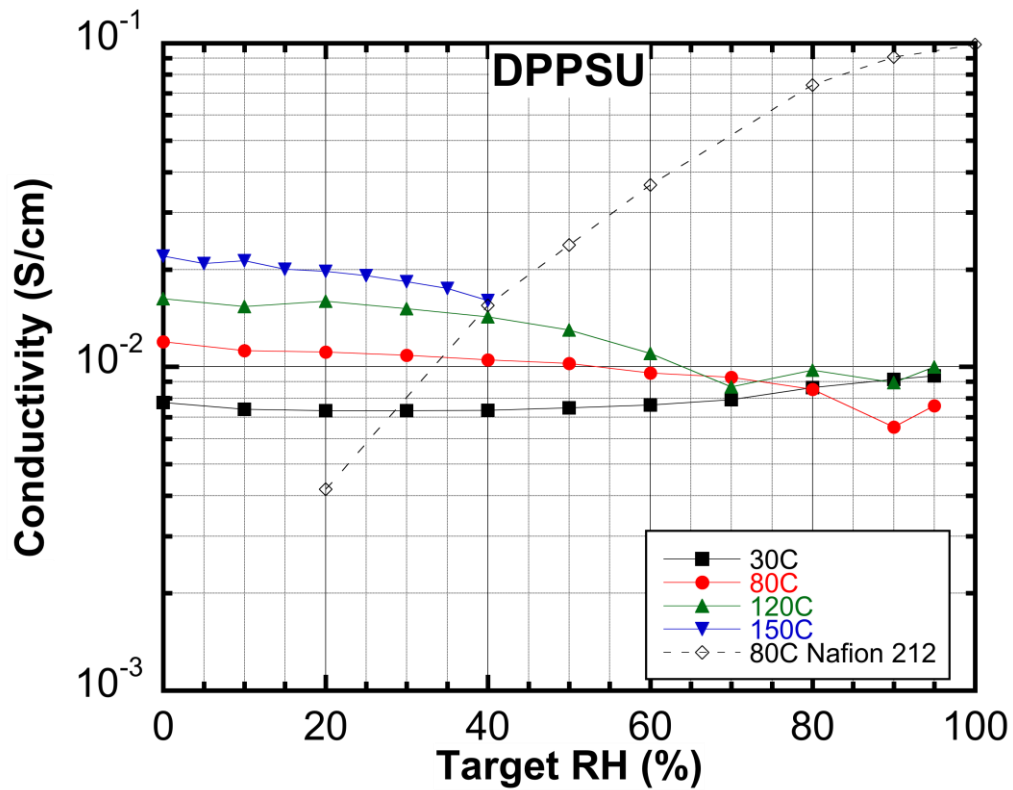


Figure 6. Through plane conductivity of DPPSU showing minimal dependence on RH as compared to Nafion 212 (dashed line)

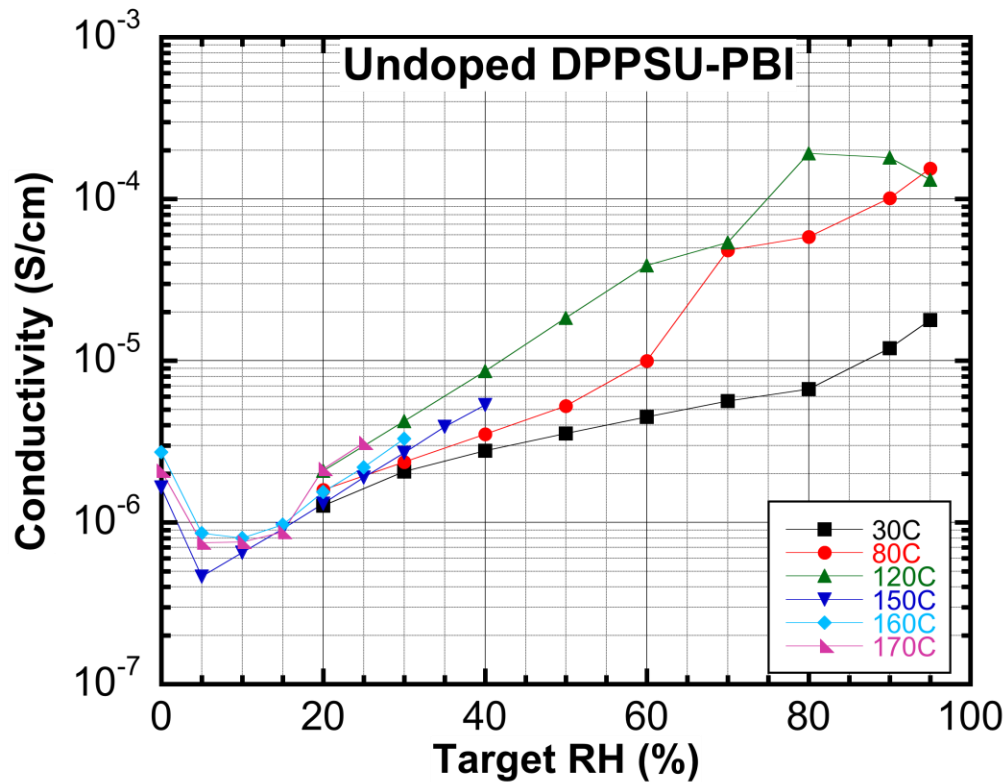


Figure 7. Through plane conductivity of DPPSU-PBI blend showing significant reduction in conductivity and the appearance of RH dependence.

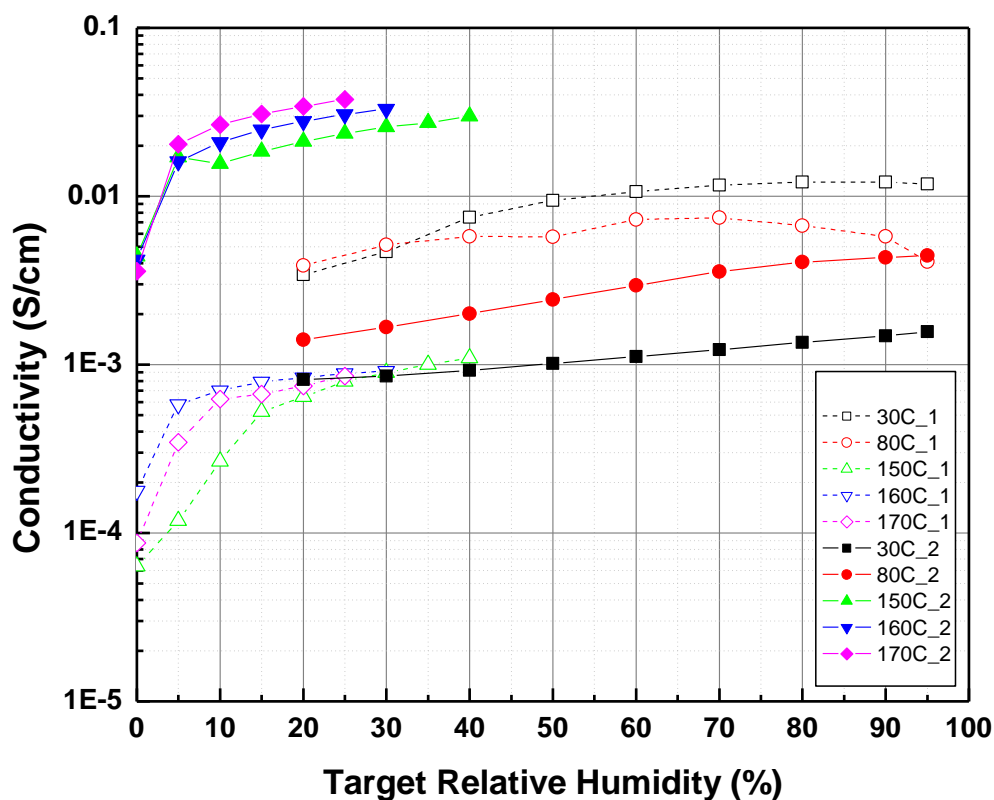


Figure 8. Through plane conductivity of H_3PO_4 doped DPPSU-PBI. Sample 1 (dashed line) was tested following the temperature sequence 30, 80, 150, 160, 170°C. Sample 2 (solid line) was tested following the temperature sequence 150, 160, 170, 30, 80°C.

Conclusion

In this study, polysulfone was modified by bromomethylation and phosphonation to contain 200% phosphonation and blended with polybenzimidazole to study the potential of this polymer as the electrolyte membrane in PEM fuel cells. The DPPSU membrane shows conductivity of 2×10^{-2} S/cm at 170°C in dry conditions and H_3PO_4 doped DPPSU-PBI shows conductivity of 4×10^{-2} S/cm at 170°C in dry conditions. The loss of phosphoric acid during temperature and humidity cycling requires further study on the durability of these membranes in a fuel cell environment. However, the high conductivity of these polymers is promising for their use in high temperature PEM fuel cells.

Acknowledgement

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