

An investigation of proton conductivity of binary matrices sulfonated polysulfone/polyvinyltriazole after doping with inorganic acids

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Abstract. As anhydrous proton conductive membranes, sulfonated polysulfone (SPSU) and polyvinyl triazole were studied as binary matrices. The sulfonation of polysulfone was performed with trimethylsilylchlorosulfonate and high degree of sulfonation (140%) was obtained. Ion exchange capacity of SPSU was determined as 3.05 mmol⁻¹/g. The polymer electrolyte membranes were prepared by blending of sulfonated polysulfone with polyvinyl triazole and phosphoric acid. Fourier transform infrared spectroscopy confirmed the sulfonation of the polysulfone and the ionic interaction between sulfonic acid and triazole units. Thermogravimetric analysis showed that the polymer electrolyte membranes are thermally stable up to at least 150°C. Scanning electron microscopy analysis indicated the homogeneity of the ternary composites. The maximum proton conductivity has been measured as 3.63 × 10⁻⁴ S cm⁻¹ at 150°C.

Keywords. Sulfonated polysulfone; polyvinyl triazole; polymer electrolyte; proton conductivity; composite membrane.

1. Introduction

Proton-conducting polymers are attractive materials owing to their potential applications in proton exchange membrane fuel cells (PEMFCs), electrochromic devices (ECDs) and supercapacitor.^{1–3} A perfluorosulfonic acid-type polymer, Nafion, is currently used as the polymer electrolyte in PEMFCs. It has hydrophilic and hydrophobic regions, and the proton transfer occurs *via* water molecules present in their hydrophilic channels. Several functional polymers were produced to produce alternative polymer matrices to Nafion. Among several sulfonated systems,^{4–8} polystyrene⁴ and polysulfone⁵ are mostly used as homopolymer or composites. These acidic polymers have high water uptake and if used as humidified condition their usage are limited to 100°C. Therefore alternative, materials such as benzimidazole,⁶ imidazole⁷ and triazole⁸ were intercalated in these acidic polymers to provide proton conduction at high temperature. In addition, they are also blended with polyvinyl imidazole⁹ and polyvinyl triazole.¹⁰

Sulfonated polysulfone (SPSU) is one of the acid functional polymers that is produced with chemical sulfonation of polysulfones which are known with their high thermal, chemical and mechanical stability.¹¹ SPSU can be used as proton conductive membrane if it is highly sulfonated and has high water uptake property.^{11,12} The proton conductivity

of the SPSU membranes was reported as 10⁻² S cm⁻¹ at 80°C¹³ and 3.2 × 10⁻² S cm⁻¹ at 90°C.¹⁴ Moreover, the SPSU membranes have lower gas permeability and liquid (water and methanol) permeability than the sulfonated perfluorinated ionomers.¹⁵

Although SPSU was mostly used in humidified systems, there are studies about its usage in anhydrous membranes. For this purpose SPSU was previously doped with a heterocyclic compound, 1*H*-1,2,3-benzotriazole and high proton conductivity was reported.¹⁶ In this study, SPSU was blended with polyvinyl triazole (PVTri), which has high proton transfer capability with triazole group in each repeating unit. Several composite membranes of PVTri were previously reported such as polyvinyl phosphonic acid¹⁷ and polystyrene sulfonic acid.¹⁸ The proton conductivity of these composite membranes were analysed both in humidified and anhydrous states.^{17,18}

In our work, the SPSU was synthesized with high degree of sulfonation using trimethylsilylchlorosulfonate (TMSCS) as sulfonating agent. The proton conductive membranes were prepared by blending SPSU, polyvinyl triazole and phosphoric acid (PA) at several molar ratios. Homogeneous and free standing membranes were obtained and characterized with Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC) and scanning electron microscopy (SEM). The effect of polyvinyl triazole and phosphoric acid on proton conductivity was investigated with impedance analyzer.

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2. Experimental

2.1 Materials and preparation

The commercial polysulfone (PSU; Aldrich), TMSCS; (Aldrich), 1,2-dichloroethane (DCE; Merck), methanol (Sigma-Aldrich), dimethylformamide (DMF; Merck), 1-vinyl-1,2,4-triazole (>97%, Fluka), orthophosphoric acid (>99%, Merck) and toluene (>99%, Merck) were used as received. Azobisisobutyronitrile (AIBN; Merck) was recrystallized from THF prior to use. Poly(1-vinyl-1,2,4-triazole) (figure 1) was produced by free radical polymerization of 1-vinyl-1,2,4-triazole in toluene using AIBN (1 mol%) as initiator. The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 85°C for 2 h. The resulting polymer was precipitated as white powder and filtered and washed several times with toluene. PVTri was dried in vacuum and stored in the glove box. SPSU (figure 1) was prepared according to the literature.¹² The commercial polysulfone (0.1 mol) was dissolved in 1,2-dichloroethane at 25°C for 4 h under nitrogen atmosphere. Trimethylsilylchlorosulfonate (0.15 mol) was added at room temperature as the sulfonation agent. During the reaction, N₂ was purged continuously through the reaction solution and HCl was continuously produced and released out of the reactor with N₂. After about 36 h, methanol was added to quench the reaction, and to cleave the silyl sulfonate moieties yielding SPSU. Silicon-containing compounds, methyl sulfate, dichloroethane, methanol and water were removed through evaporation first at 1 atm and then vacuum (400 mmHg) at the temperature of 55°C.¹⁶ The resulting SPSU is soluble in methanol and DMF.

Ion exchange capacity (IEC) of SPSU was determined by volumetric titration according to literature.¹⁹ The sample was immersed and stirred in 20 ml of 0.10 M NaOH/1.0 M NaCl mixed aqueous solution (1/4 by volume) for 24 h at room temperature. Subsequently, 10 ml of 0.10 N HCl solution was added, and the excess amount of HCl was back titrated with 0.025 N NaOH aqueous solution in the presence of phenolphthalein indicator. The IEC value (mmol g⁻¹) of the samples was calculated using

$$\text{IEC} = 0.025 \times (V_{\text{NaOH}} - V_{\text{B}}) / W_{\text{dry}}, \quad (1)$$

where V_{NaOH} is the volume of 0.025 N NaOH aqueous solutions for the volumetric titration, V_{B} the volume of the NaOH aqueous solution for blank titration, and W_{dry} the dry weight of the samples.¹⁹

Using this method the IEC value of SPSU was determined as 3.05 mmol g⁻¹, which indicates that the degree of sulfonation (DS) is about 140% [(mol SO₃H/repeat unit) × 100].

Proton conductive composite membranes were prepared by blending of SPSU with polyvinyl triazole and H₃PO₄. A stoichiometric amount of SPSU, PVTri and H₃PO₄ were admixed in DMF with several mol ratios ($X = 0.5, 1, 2$ and 4) for 5 h at 50°C. The membrane was then prepared by casting of the solutions on a polished poly(tetrafluoroethylene), and the solvent was slowly evaporated at 50°C for 24 h. To ensure complete solvent removal, the membranes were placed under vacuum 200 mmHg at 50°C. Homogeneous and free standing membranes were obtained.

2.2 Characterizations

FT-IR spectra were recorded on a Bruker a-P in ATR in range of 4000–400 cm⁻¹.

Thermal stabilities of the polymer electrolytes were examined by TG analyses with a Perkin-Elmer STA 6000. The samples (~10 mg) were heated from room temperature to 700°C under N₂ atmosphere at a scanning rate of 10°C min⁻¹.

DSC measurements were carried out on a Perkin-Elmer JADE DSC under nitrogen atmosphere and heating-cooling curves were recorded at a rate of 10°C min⁻¹.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The films were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1 Hz–3 MHz at 10°C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between –100 and 250°C.

The morphology of the membranes was observed by SEM type JEOL 7001 FESEM. The samples were previously coated with gold in a sputtering device.

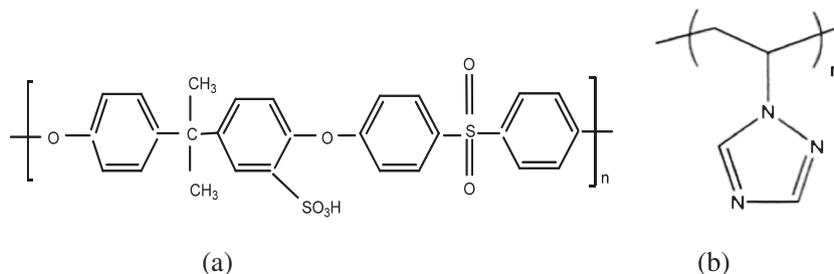


Figure 1. Molecular structures of (a) sulfonated polysulfone and (b) polyvinyltriazole.

3. Results and discussion

3.1 FT-IR studies

Figure 2 shows the FT-IR spectra of pure polysulfone, SPSU, PVTri and SPSU–PVTriX–PAX composite membranes. SPSU has peaks at 687, 1015, 1100, 1150, 1240, 1483, 2970, 3070 and 3440 cm^{-1} that corresponds to C–S, SO_3 , C–O, R– SO_2 –R, C–O, C=C (aromatic), CH (aliphatic), CH (aromatic) and OH stretching bonds, respectively.^{20–22} When compared with FT-IR of PSU, the presence of –OH peaks at 3500 cm^{-1} symmetric and asymmetric vibrations of SO_3H groups at 1156 and 1302 cm^{-1} and also O=S=O stretching vibration of – SO_3 groups near 1015 cm^{-1} in FT-IR of SPSU confirm the sulfonation of PSU.²³ PVTri has C–N and C=N stretchings at 1430–1650 cm^{-1} range and N–N stretching at 1270 cm^{-1} .²⁴ In the ternary composites there is a bond at 1665 cm^{-1} due to N–H bending vibration of acid-protonated triazole rings. Between 3500 and 2000 a broadening of the band can be related to hydrogen bonding network formation. Within 1800–900 cm^{-1} region, the peaks near 1100 and 975 cm^{-1} are attributed to characteristic absorptions of HPO_4^{2-} and H_2PO_4^- in the blends and they increase with PA content.²⁵

3.2 Thermal analysis

Figure 3 shows the thermogravimetric analysis of PSU, SPSU, PVTri and SPSU–PVTriX–PAX composites. Pure PSU is thermally stable up to 500°C and then major weight loss occurs due to degradation of the polymeric backbone.¹⁴ The TGA curve of SPSU has two weight loss region, where 30% weight loss occurs between 200 and 350°C due to degradation of sulfonic acid groups and the degradation of polymer backbone occurs above 500°C.^{22,26} This distinct change in TGA curve also verifies the sulfonation of PSU. PVTri homopolymer is thermally stable up to 350°C and the major weight loss derives from the

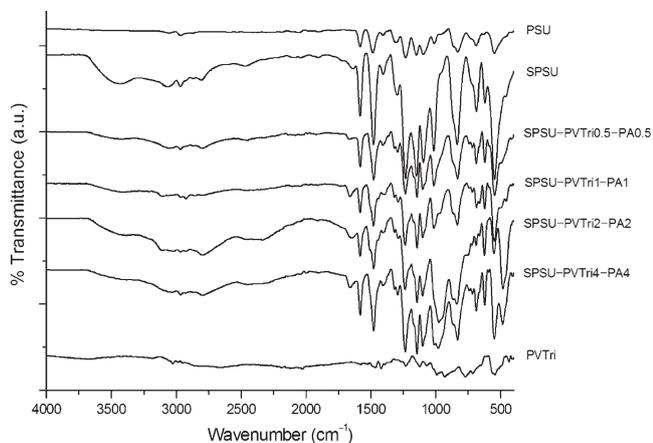


Figure 2. FT-IR spectra of PSU, SPSU, PVTri and SPSU–PVTriX–PAX ($X = 0.5, 1, 2, 4$) membranes.

thermal decomposition of the side groups and polymer main chain. The minor (10%) weight loss up to 200°C may be attributed to the absorbed humidity. The ternary composites can be said to be thermally stable up to at least 150°C and decomposition temperature decreases with H_3PO_4 content as expected.

DSC curves of SPSU and SPSU–PVTriX–PAX are given in figure 4. Pure PSU and PVTri are reported to have T_g of 185 and 165°C, respectively.^{16,24} After sulfonation the T_g decreased to 120°C. SPSU–PVTriX–PAX blends showed glass transition (T_g) temperatures of 115, 108, 100 and 97°C for $X = 0.5, 1, 2, 4$, respectively. The ternary blends have T_g values lower than pure PVTri and SPSU, which is due to plasticizing effect of PA.

3.3 Morphology

The morphology study is important to confirm the homogeneity of polymer–polymer blends. In this work, SPSU–PVTriX–PAX membranes are observed to be more homogeneous compared to SPSU–PVTri blends. Figure 5 shows SEM of the ternary composites. The membranes exhibit single-phase formation, which shows that the PVTri and H_3PO_4 uniformly distributed into the polysulfone matrix and there is no agglomeration or phase separation at micrometre and nanometre scale level. In figure 5d we observe many cracks in nm scale, which is related with the drying procedure and has no effect on the proton conductivity or thermal properties.

3.4 Conductivity measurement

The frequency-dependent AC conductivities, $\sigma_{AC}(\omega)$ of the polymer electrolyte membranes were calculated at different temperatures using

$$\sigma'(\omega) = \sigma_{AC}(\omega) = \varepsilon''(\omega)\omega\varepsilon_0, \quad (2)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ the angular frequency, ε_0 the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14} \text{ F cm}^{-1}$), and ε'' the imaginary part of complex dielectric permittivity (ε^*). The proton conductivities of anhydrous polymer electrolytes were measured from 20 to 150°C.

Figure 6 shows the AC conductivity of SPSU–PVTriX–PA4 vs. log frequency at several temperatures. The conductivity increases with the temperature and the DC conductivity (σ_{DC}) of the samples was derived from the plateaus of σ_{AC} vs. log frequency by linear fitting of the data. The DC conductivities of SPSU–PVTriX and SPSU–PVTriX–PAX are compared in figure 7. It is clear that the DC conductivity strongly depends on the temperature, PVTri and H_3PO_4 ratio. The maximum proton conductivity was obtained as 2.5×10^{-4} and $2.3 \times 10^{-4} \text{ S cm}^{-1}$ for SPSU–PVTri4–PA4 and SPSU–PVTri2–PA2, respectively, at 150°C.

As SPSU has high thermal stability, good mechanical and film forming property, it was studied by different groups

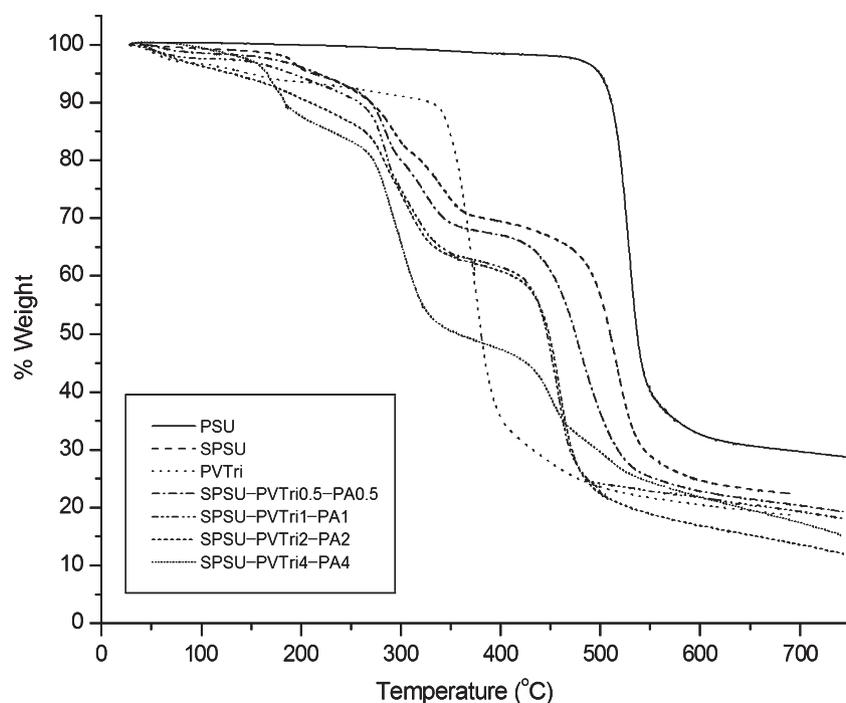


Figure 3. TGA curves of PSU, SPSU, PVTri and SPSU-PVTriX-PAx ($X = 0.5, 1, 2, 4$) electrolytes at a heating rate of $10^{\circ}\text{C min}^{-1}$.

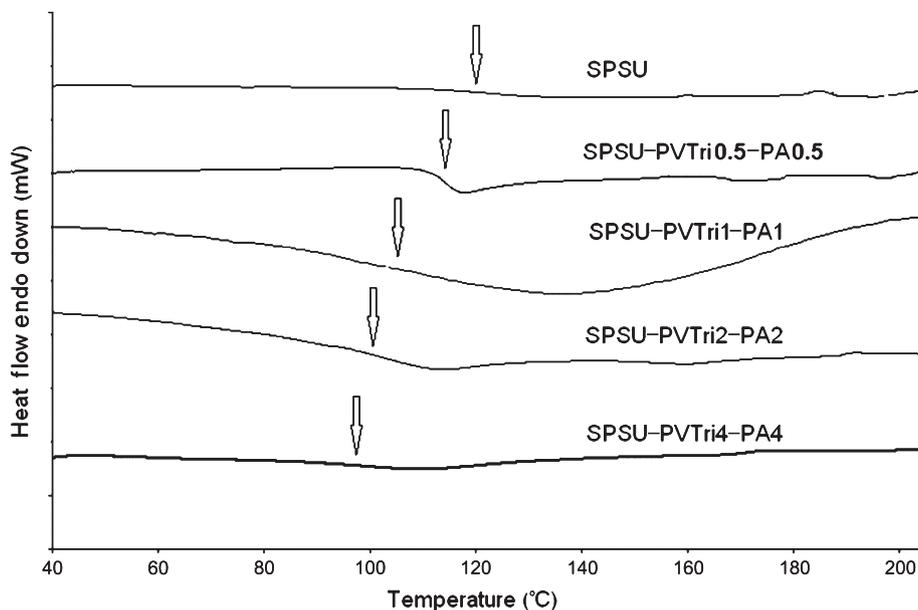


Figure 4. DSC curves of SPSU and SPSU-PVTriX-PAx ($X = 0.5, 1, 2, 4$) electrolytes at a heating rate of $10^{\circ}\text{C min}^{-1}$.

as proton conductive material but most of them are in humidified condition.^{12,22} SPSU/1*H*-1,2,3-triazole composite membranes were reported as anhydrous system, but the system produced considerable proton conductivity at very high dopant ratios.²⁷ Manthiram and co-workers immobilized 5-aminobenzotriazole to polysulfone and after blending with sulfonated poly(ether ether ketone) they investigated the

proton conductivity and obtained values around $10^{-4} \text{ S cm}^{-1}$ in anhydrous conditions.^{28,29} In another study, phosphoantimonic acid was intercalated into SPSU and after humidification they investigated the proton conductivity.³⁰ Previously we studied SPSU/benzotriazole system, which resulted in high proton conductivity at lower dopant ratios.¹⁶ In order to be used in anhydrous conditions, SPSU may be blended with

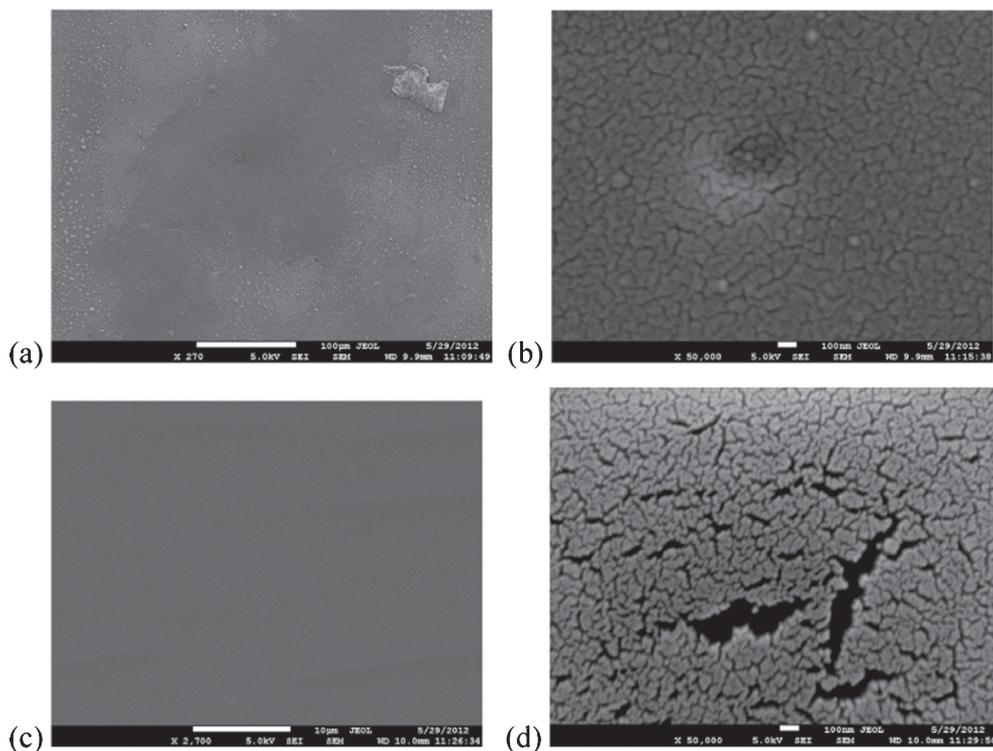


Figure 5. SEM images of (a and b) SPSU-PVTri1-PA1 and (c and d) SPSU-PVTri2-PA2 membranes.

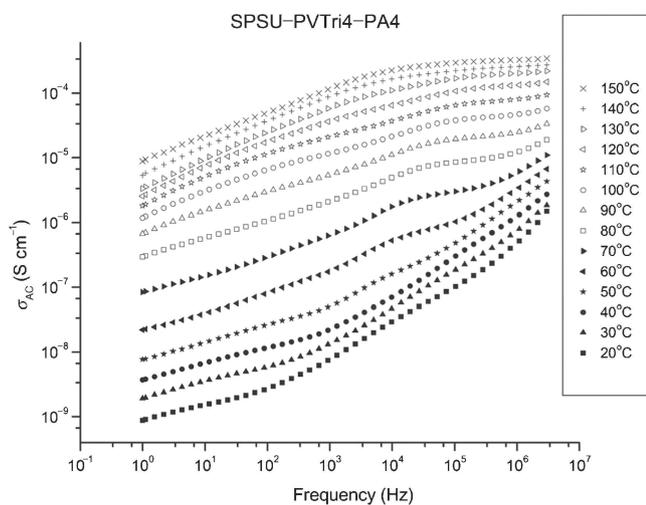


Figure 6. AC conductivity of SPSU-PVTri4-PA4 vs. log frequency (Hz) at various temperatures.

azole-containing polymer and the resulting channel between polymers may be filled with high proton conductive solvent such as PA.

In this work polysulfone was sulfonated with high ratio (140%) and blended with polyvinyl triazole. Here polyvinyl triazole is considered to make ionic interaction with sulfonic acid units of SPSU. The binary mixtures resulted in less homogeneous membrane and also low proton conductivity, which may be due to ionic crosslink that limit the proton

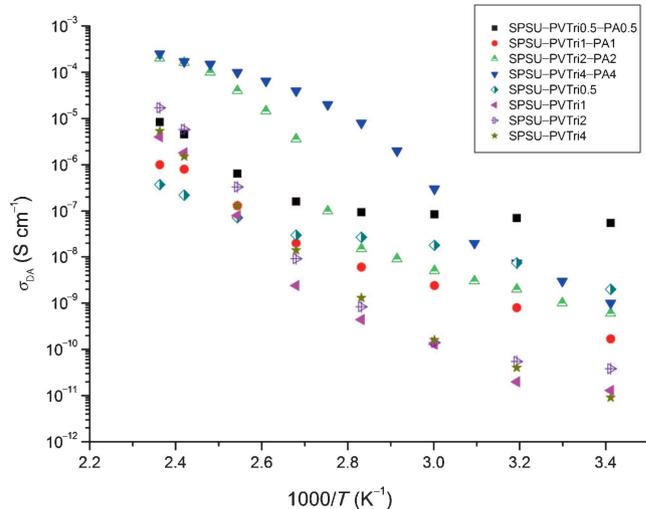


Figure 7. DC conductivities of SPSU-PVTriX and SPSU-PVTriX-PAx ($X = 0.5, 1, 2, 4$) as a function of reciprocal temperature.

transfer in the matrix.^{6,18} Therefore, ternary membranes were prepared by homogeneous solution doping of SPSU/PVTri with H_3PO_4 . Here homogeneous membranes were obtained and proton conductivity increased to $2.5 \times 10^{-4} \text{ S cm}^{-1}$ at 150°C for SPSU-PVTri4-PA4. For this ternary composite the proton transfer path can be explained as Grotthuss mechanism, where sulfonic acid and PA groups protonates free nitrogens in PVTri and proton transfer occurs between protonated and non-protonated

nitrogens in heterocyclic group and also sulfonate and phosphate groups.² At higher doping ratios, the DC conductivity curves show VTF (Vogel–Tamman–Fulcher) behaviour, which indicates the contribution of segmental motions on the proton conductivity in these novel matrices.

4. Conclusions

In the present work, SPSU was produced with high sulfonation ratio using trimethylsilylchlorosulfonate as sulfonating agent. Both direct titration and ion exchange capacity measurements indicated a degree of sulfonation of 140%. The polymer electrolyte membranes were prepared by blending of SPSU with polyvinyl triazole and PA. The ionic interaction between acidic groups and polyvinyl triazole was proved by FT-IR spectroscopy. Thermogravimetric analysis showed that the materials are thermally stable up to at least 150°C. The proton conductivity of these materials increased with the increase in polyvinyl triazole and PA contents. The maximum proton conductivity was measured for SPSU–PVTri4–PA4 as 2.5×10^{-4} S cm⁻¹ at 150°C in anhydrous condition. In that matrix the presence of PA provided homogeneity and also form a proton transfer path inside the polymer matrix. The material can be used as membrane in high-temperature PEMFC applications.

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