Nafion/poly(1-vinyl-1,2,4-triazole) blends as proton conducting membranes for polymer electrolyte membrane fuel cells

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ABSTRACT

In this study, proton conducting Nafion–poly(1-vinyl-1,2,4-triazole) blends are produced. Nafion/polymer blend membranes are prepared by means of film casting from the Nafion–PVTri solutions at several molar ratios of PVTri repeat unit to –SO_3H. The chemical structure of the homopolymer PVTri is confirmed by FT-IR and ^{13}C NMR. Thermal properties are investigated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and the results illustrated that all these Nafion–PVTri electrolytes are thermally stable at least up to 300 °C. The membrane properties are further characterized for their morphology by scanning electron microscopy (SEM) and water uptake measurements. The methanol permeability of these membranes is measured and the results exhibited that they have quite lower methanol permeability compared to pristine Nafion112. The electrochemical properties of PVTri are investigated by cyclic voltammetry. The conductivity of Nafion–P(VTri)$_1$ blend membranes is measured to be $5.3 \times 10^{-4}\,S\,cm^{-1}$ at 220 °C, in anhydrous state. The conductivity of blend increased at least three orders of magnitude up on hydration, i.e., exceeding $10^{-3}\,S\,cm^{-1}$ with RH = 50% at ambient temperature.

1. Introduction

There is an extensive research for the development of proper membranes for polymer electrolyte membrane fuel cell (PEMFC) application. Perfluorosulfonic acid membranes (e.g., Nafion) is commonly used polyelectrolyte which have high chemical stability and provide high proton conductivity in fully hydrated state. Besides its high cost, a major weakness of Nafion is the low proton conductivity under low humidity condition, which leads to poor fuel cell performance at higher temperatures (1,2(. Thus there is strong requirement for proton conducting polymer electrolytes that can maintain high proton conductivity at low humidity contents. Working at higher temperatures (100–200 °C) brings some advantages such as CO tolerance, easier heat and water management, faster electrode kinetic and high energy efficiency [3,4]. Therefore the development of anhydrous proton conducting membranes became necessary due to its stability against hydration and dehydration and ability to conduct protons over the non-aqueous phase. Alongside, a variety of alternative approaches have been emerged to search water-free polymer electrolyte systems with sufficient proton conductivity at higher temperatures (T > 100 °C). The previous approach was the polymer acid complexes where the several promising systems based on PBI/H_3PO_4 have been reported (5–7(. In acid doped polymer electrolytes the structural diffusion is predominant where the proton diffusion is mainly controlled by proton transport among acidic units (1(. It was reported that the incorporation of phosphoric acid within Nafion yielded a super acid under anhydrous conditions where the charged species are generated yielding excess $H_4PO_4^+$ and an immobilized –SO_3^- anion (8(. The self-ionization of the phosphoric acid is reduced, yielding a lower concentration of the $H_2PO_4^-$ ion. Then the proton transport through structure diffusion is reduced (8(.

To solve the problem, aromatic heterocyclic proton solvents which enable proton diffusion at higher temperatures were impregnated into hydrophilic channels of perfluorosulfonic acid. Several works have been already been reported to modify the Nafion membrane. In this context, liquid solvents such as triazole, amino triazole, imidazole, butyl methyl imidazolium triflate, and benzimidazole performed the function of water in proton conduction with improved physical characteristics, i.e., mechanical properties, low volatility of proton solvent, etc. [9–14]. Although the use of these heterocyclic systems as composite components in an acidic polyelectrolyte was useful for the development of high temperature resistant films, the solvent leaching out could be problem for prolonged fuel cell application. Alternatively, Nafion/polymer blends have been reported claiming to reduce methanol permeability and reduce the solvent exclusion. These systems include Nafion/PBI [15,16], sulfonated polypropy-

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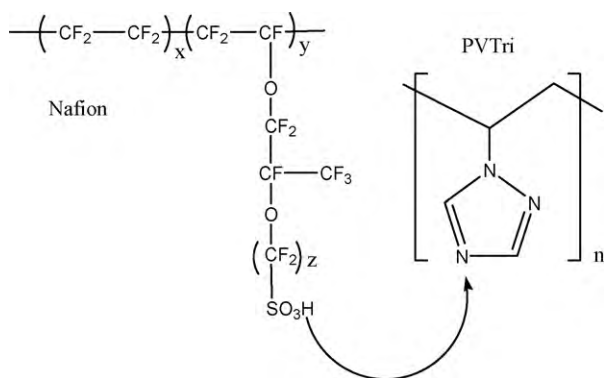
Fig. 1. Chemical structures and interaction of (a) poly(1-vinyl-1,2,4-triazole) and (b) Nafion.

Fig. 2. Transparent and thin film of Nafion–P(VTri)$_{11}$ blend membrane.

lene oxide oligomers/Nafion [17], Nafion/poly(aryl ether ketone) [18] and PEO–PPO–PEO triblock copolymer/Nafion blend membranes [19].

The use of poly(1-vinyl-1,2,4-triazole) (PVTri), (Fig. 1) as a blend component with Nafion would be interesting since PVTri bears triazole as repeating and showed high proton conductivity when it is doped with phosphoric acid. In addition, PVTri is thermally as well as electrochemically stable polymer and it can be used for high temperature applications [20]. The polymer blends consisting of acidic and heterocyclic polymers which may allow long range proton transport via structure diffusion.

In the present study, the homopolymer poly(1-vinyl-1,2,4-triazole) was synthesized by free radical polymerization of 1-vinyl-1,2,4-triazole. The blends were prepared by film casting from commercial Nafion® solutions and PVTri at several stoichiometric ratios n (=[PVTri repeat unit]/[SO$_3$H]). The synthesis, molecular interactions, surface morphology, thermal properties, electrochemical stability, proton conductivity, water uptake and methanol permeability results were discussed and compared with previously reported systems.

2. Experimental

2.1. Materials

Nafion solution (15%, Ionpower), 1-vinyl-1,2,4-triazole (>97%, Fluka), toluene (>99%, Merck), DMF (>99%, Alfa Aesar), hydrogen peroxide solution (30%, Riedel-de Haën) and sulfuric acid (95–97%, Riedel-de Haën) were used as received. Before using the initiator azobisisobutyronitrile (AIBN; Merck) was recrystallized from THF.

2.2. Membrane preparation

Poly(1-vinyl-1,2,4-triazole), PVTri, was produced by free radical polymerization of 1-vinyl-1,2,4-triazole in toluene using AIBN (1 mol %) as initiator [20]. The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 85 °C for 2 h. The resulting white powder polymer was filtered and dried in vacuum. The reaction yield was about 85% and the polymer was soluble in water and common organic solvents.

PVTri was dissolved in DMF and mixed with commercial Nafion solution (15%) at several molar ratios with respect to sulfonic acid to triazole repeat unit. The solutions were stirred until they are homogeneous and then they were cast on a polished Teflon plates. The solvent was slowly evaporated at 40 °C, which is followed by drying under vacuum at 80 °C for at least 24 h. Transparent, hygroscopic and free standing films were produced and they stored in the glove box for characterizations (Fig. 2). The samples were denoted as Nafion–P(VTri)$_n$ where the n is the mole ratio of tria-

zole to –SO$_3$H. Thicknesses of the films were ranged from 150 to 300 μm.

2.3. Characterizations

Chemical structures of homopolymer PVTri was confirmed by Solid state ^{13}C CP-MAS NMR using 700 MHz Bruker Avance spectrometer. The vibration properties of the blend electrolytes were investigated with a Bruker Alpha Fourier Transform Infrared (FT-IR) spectrometer using the attenuated total reflection (ATR) technique.

The thermal stability of the materials was measured by using thermogravimetric analysis (TGA) using Mettler-Toledo. The samples were heated from room temperature to 700 °C at rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler-Toledo under argon atmosphere. The samples were heated and cooled between room temperature and 200 °C at rate of 10 °C min^{-1} and second heating curves were evaluated.

The surface morphology of blend membranes was investigated by scanning electron microscopy (SEM, Philips XL30S-FEG). All of the samples were sputtered with gold for 150 s before SEM measurements.

Water uptake experiments were made to compare the swelling properties of Nafion and blend membranes. Dried membranes were soaked in water and equilibrated at 25 °C. Water uptake (W) was calculated in weight percent according to $W = 100 \times (m_{wet} - m_{dry})/m_{dry}$ where m_{wet} and m_{dry} are the weight of the wet and dry membranes, respectively.

Methanol permeability was measured using our homemade diaphragm diffusion cell with a volume of 4 ml (Fig. 3) [21]. The cell was filled with 2 ml pure methanol. Methanol vapor in equilibrium with the liquid diffused along the concentration gradient through the membrane, which was clamped between the mouth of glass and the cap. The cap has a hole with a 0.84 cm diameter so that the methanol diffused through the membrane could escape. The weight loss is recorded as a function of time and the data were used for permeability calculations.

Electrochemical properties of PVTri were studied with a potentiostat (Pine Instrument Model AFCBP1) in 0.1 mol dm^{-3} solution of tetraethylammonium tetrafluoroborate (TEABF$_4$) salt in acetonitrile (ACN). The CV cell consists of a platinum working electrode, Ag/Ag$^+$ reference electrode and platinum counter electrode. The solution was purged with dry nitrogen to obtain inert atmosphere. Scans were performed at 50 mV s^{-1} between a potential window of −3.20 to 1.48 for 5×10^{-3} M of PVTri.

The proton conductivity studies of the samples were performed using a Novocontrol Alpha-N high resolution dielectric analyzer.

Fig. 3. Methanol permeability diaphragm diffusion cell.

The films were sandwiched between platinum blocking electrodes and conductivity was measured in the frequency range from 1 Hz to 3 MHz as a function of temperature which was varied from 20 to 220 °C with 10 °C intervals.

3. Results and discussion

After solvent evaporation transparent films were obtained from solution cast method. The stiffness of the final membrane increased with increasing the PVTri content which was attributed to ionic complexation. Although pristine PVTri is soluble in water, Nafion–PVTri blend membranes are insoluble in water due to inter-polymer ionic complexation. Water uptake experiments demonstrated that there was no leaching out of PVTri upon swelling in excess water.

3.1. Solid state ^{13}C CP-MAS NMR spectroscopy

The solid state ^{13}C CP-MAS NMR spectrum of PVTri was shown in Fig. 4. The characteristic C peaks of the triazole ring are near 145 and 155 ppm and the signals corresponding to the C of the polymer backbone appear at 40 and 55 ppm.

3.2. FT-IR spectroscopy

The molecular structures of the Nafion/polymer blend membranes were characterized by FT-IR spectroscopy. Fig. 5 shows the FT-IR spectra of the Nafion–PVTri blend membranes and PVTri homopolymer. The triazole rings of the pristine polymer, PVTri, give rise to several medium or strong peaks in the 1430–1650 cm^{-1} range due to ring stretching (C–N, C=N) vibrations. The peak at 1270 cm^{-1} is due to the ring N–N stretching. The broad peak centered at 3430 cm^{-1} was assigned to O–H vibration of molecular
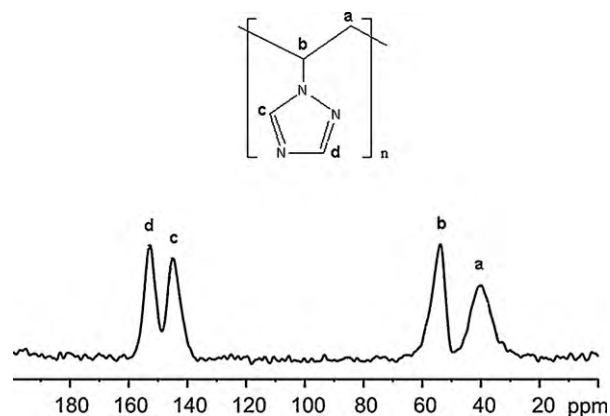

Fig. 4. Solid state ^{13}C CP-MAS NMR spectrum of PVTri.

water interacting with the pristine PVTri. In the literature, the characteristic Nafion peaks were observed at 1365 cm^{-1} (SO$_3$H), 1052 cm^{-1} (SO$_3{}^-$) and 1140 cm^{-1} (C–F) which are also illustrated in Fig. 5 [12,22]. In the blend membranes, the intensities of the bands corresponding to the azole ring between 1400 cm^{-1} and 1650 cm^{-1} have changed due to proton exchange reaction between Nafion and PVTri [23]. The protonation of the free nitrogen in the ring can also be confirmed by the peaks located near 3100 cm^{-1} [24]. The characteristic absorption bands of the samples are summarized in Table 1.

3.3. Thermal analysis

Polymer electrolyte membranes that maintain stable proton conductivity at elevated temperatures are required for PEMFC applications. Operation of a PEMFC at high temperatures have several advantages, i.e., increase in kinetic rates for the cell reaction, reduction of problems related to catalyst poisoning etc. Therefore thermal stability of the proton conducting polymer membranes is very important during applications. Previously, the thermal stability of the perfluorosulfonic acid polymers with an equivalent molecular weight of 1100 was studied by several groups [25]. They reported that weight change up to 280 °C was only due to water, while above 300 °C sulfonic acid groups start to lose. Fig. 6 shows thermogravimetry curves of Nafion–PVTri blend membranes and PVTri. The pristine PVTri has a considerable thermal stability
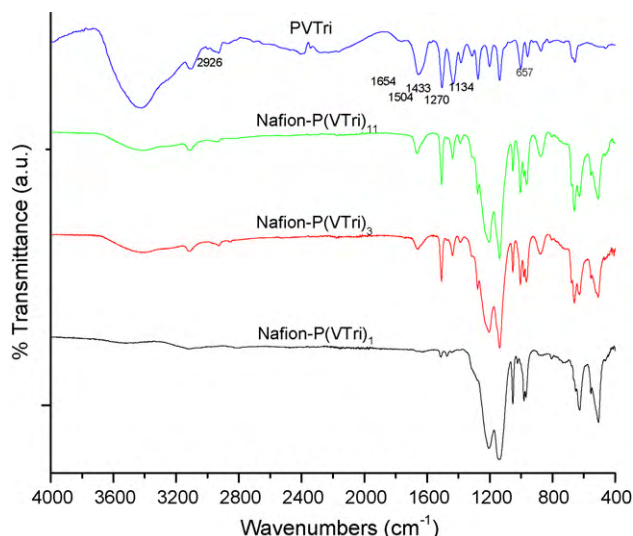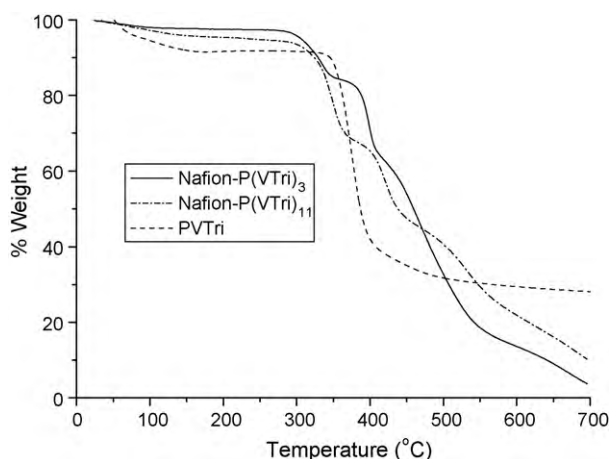

Fig. 5. FT-IR spectra of Nafion–PVTri blend membranes and pristine PVTri.

Table 1
Infrared absorption bands for Nafion–PVTri blend membranes.

Wavenumbers (cm^{-1})	Attributions
3400–3300	υ(N–H)
1659	δ(N–H)
1499	υ(C=N)
1432	υ(C–N)
1365	υ(SO$_3$H)
1272	υ(N=N)
1140	υ(C–F)
1052	υ(SO$_3{}^-$)
1410	υ(S=O)
1302	υ(C–F)
1200, 1144	υ(F–C–F)
981	υ(C–F) of –CF$_2$–CF(CF$_3$)–
967	υ(C–O–C)
851	υ(S–OH) of SO$_3$H

Fig. 6. TG thermograms of Nafion–PVTri blend membranes and PVTri at a heating rate of 10 °C min^{-1}.

Fig. 7. DSC traces of PVTri, Nafion–P(VTri)$_1$, Nafion–P(VTri)$_3$ and Nafion–P(VTri)$_{11}$ recorded in an inert atmosphere at a heating rate of 10 °C min^{-1}.

under inert conditions. For the homopolymer, the exponential weight decay until 200 °C can be attributed to absorbed humidity. Above 350 °C a remarkable weight loss derives from the thermal decomposition of the side groups and polymer main chain. The insertion PVTri into Nafion increased the thermal stability of the membranes. Initial elusive weight change may correspond to the absorbed humidity of membranes during the carrying and transferring procedures. Clearly, all the Nafion–P(VTri)$_n$ blend membranes decompose above 300 °C.

The thermal properties of the blend membranes were further investigated by differential scanning calorimetry, DSC (Fig. 7). Although the homopolymer, PVTri exhibits a glass transition at around 165 °C, Nafion–PVTri membranes showed no glass transition up to 200 °C. The reason can be attributed to proton exchange reaction between azole units of PVTri and sulfonic acid groups of Nafion. These ionic interactions may restrict the segmental mobility of the PVTri which is soaked in the hydrophilic channels of Nafion.

3.4. SEM micrographs

Surface morphologies of Nafion–PVTri blend membranes were investigated by scanning electron microscopy (Fig. 8). Due to strong interaction between of sulfonic acid groups of Nafion and the triazole units of PVTri, no phase separation occurred during solvent evaporation, hence homogeneous and transparent films formed. This result is also consistent with the DSC curves of blend membranes where there is no separate T_g transition of impregnated PVTri was observed.

3.5. Water uptake

Shown in Fig. 9 is the water uptake of the blend membranes compared with Nafion. Water uptake of Nafion–P(Vri)$_1$ about 10% and that of Nafion–P(Vri)$_6$ is 48%. Clearly, the initial increase of the PVTri content in Nafion matrix decreases the water uptake. The reason can be attributed to complexation of the triazole and sulfonic acid units which decreased the swelling behavior of the membrane. On the other hand, water uptake increased by further increasing of PVTri content due to the swelling of PVTri in the Nafion matrix. In addition, the experimental results demonstrated that there was no PVTri loss upon swelling in excess water.

3.6. Methanol permeability

Methanol crossover is still an unsolved problem in direct methanol fuel cells, especially for portable applications where the current densities are relatively low. Fuel crossover at high methanol concentrations from anode side to the cathode side causes polarization losses. In this study, methanol permeability of the blend membranes was measured by simple homemade diaphragm diffusion cell similar to the study of Gasa et al. [21,26]. The cell is filled with 2 ml pure methanol and the mass flow is recorded as a function of time (Fig. 10). Molar methanol flux (J) through Nafion112 and Nafion–PVTri blends was calculated using Eq. (1). Nafion112 with known permeability is used as reference for blend membranes. Methanol permeability of blend membranes may be calculated using molar flux (J) shown in Eq. (2) [21].

$$J = \frac{W}{M_W \times A \times t} \tag{1}$$

$$\frac{J_1 l_1}{J_2 l_2} = \frac{P_1}{P_2} \tag{2}$$

where J: flux, M_W: molecular weight, W: weight loss (g), P: permeability, l: thickness (cm), A: area (cm^2), t: time (s).

Thickness of the films was taken into account leading the cancellation of the thickness values (l) in Eq. (2). Therefore, permeability is directly proportional to the molar flux. The measured methanol flux through Nafion 112 and Nafion–P(VTri)$_3$ were 2.2×10^{-9} mol cm^{-2} s^{-1} and 0.9×10^{-9} mol cm^{-2} s^{-1}, respectively. It is clearly seen that the methanol crossover in the blended membrane is at least two times lower than commercial Nafion 112. Our results are comparable with the literature [27,28].
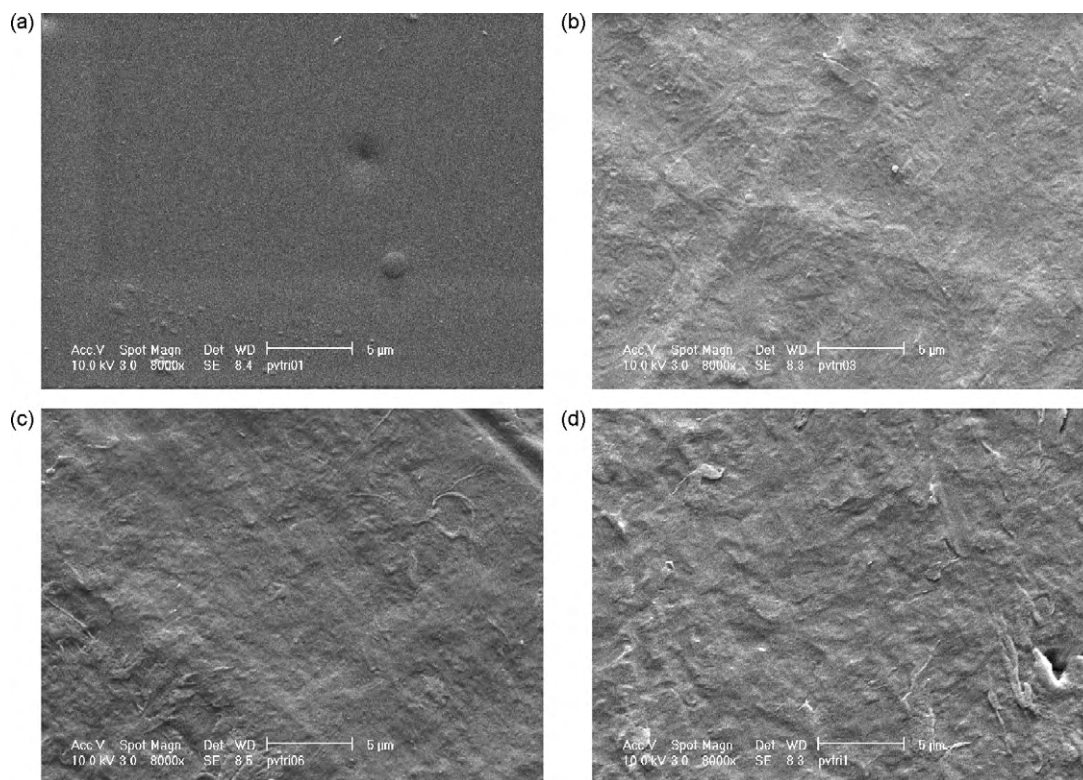
Fig. 8. SEM micrographs of the surface of (a) Nafion–P(VTri)$_1$, (b) Nafion–P(VTri)$_3$, (c) Nafion–P(VTri)$_6$ and Nafion–P(VTri)$_{11}$ blend membranes.
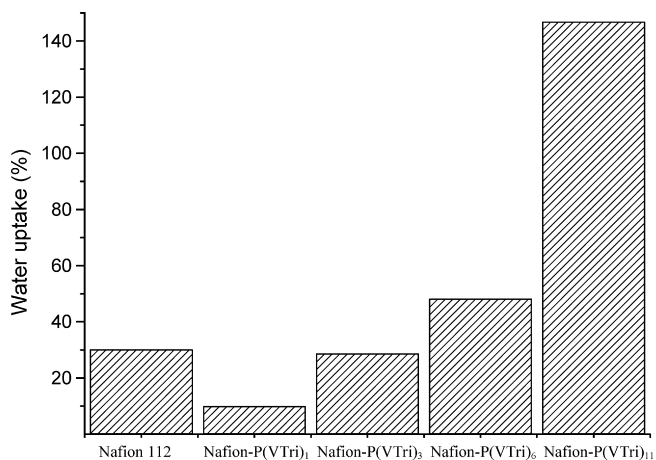

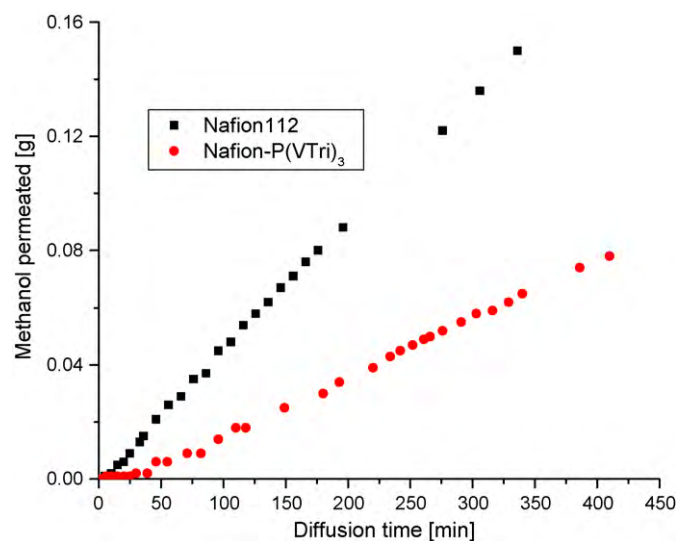**Fig. 9.** Water uptake of Nafion and blend membranes.

Fig. 10. Mass flow of methanol through pure Nafion112 and Nafion–P(VTri)$_3$ blend membranes.

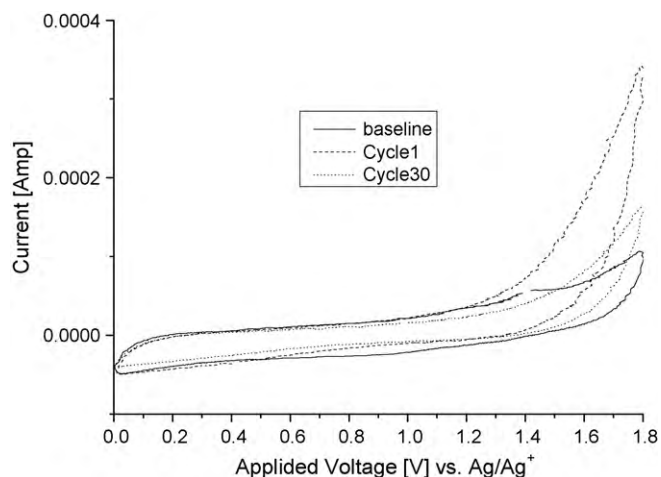### 3.7. Electrochemical stability of PVTri

Fig. 11 shows the some cyclic voltammagrams for PVTri in CH$_3$CN solution purged with N$_2$. The cyclic voltammetric measurements were performed in a typical three electrode cell containing 0.1 mol dm^{-3} CH$_3$CN solution of tetraethylammonium tetrafluoroborate and 0.5×10^{-3} M of PVTri, using platinum working electrode, platinum counter electrode, and Ag/Ag$^+$ reference electrode. No obvious redox peaks are observed in the potential range 0 to +1.8 V, indicating that PVTri can exhibit adequate electrochemical stability under the fuel cell operating conditions.

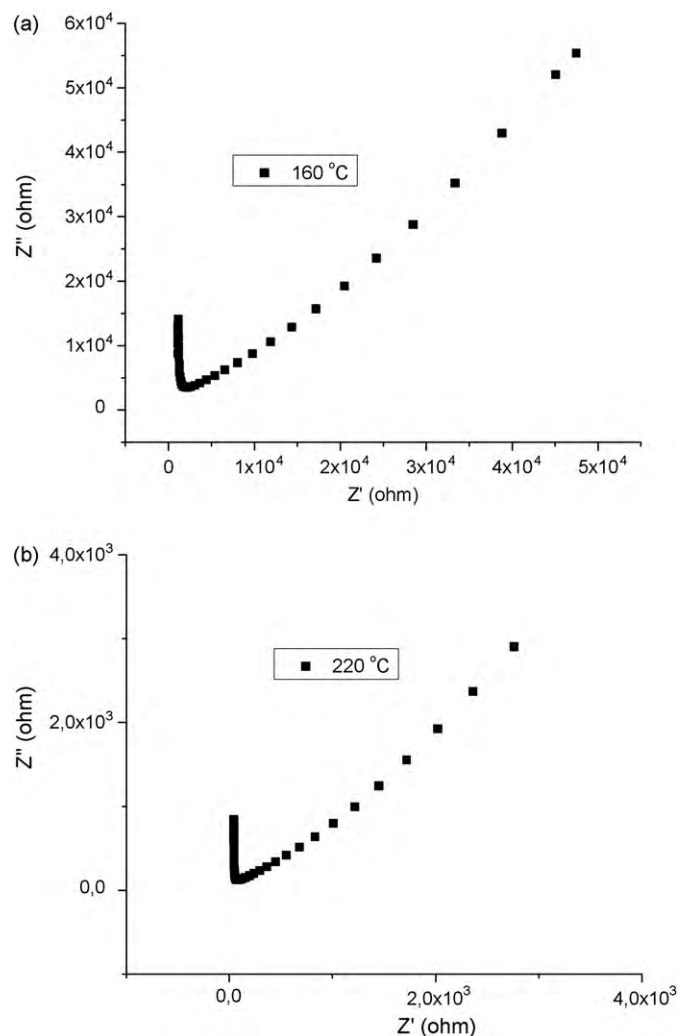### 3.8. Proton conductivity

Frequency dependent proton conductivity of the samples was measured by impedance method as a function of tem-

perature. The samples were dried under vacuum at 80 °C for at least 24 h prior to measurements. Proton conductivity of the membranes can be calculated from Cole–Cole plots, which are gained from AC impedance. Typical Cole–Cole plots of the membrane material, Nafion–P(VTri)$_1$ which were measured at 160 and 220 °C are shown in Fig. 12a and b, respectively.

The temperature dependence of proton conductivities for anhydrous Nafion–P(VTri)$_n$ systems is illustrated in Fig. 13. The conductivity of the Nafion–P(VTri)$_n$ system depends on the composition as well as the temperature. The proton conductivity of the Nafion–P(VTri)$_1$ sample is higher, especially at higher
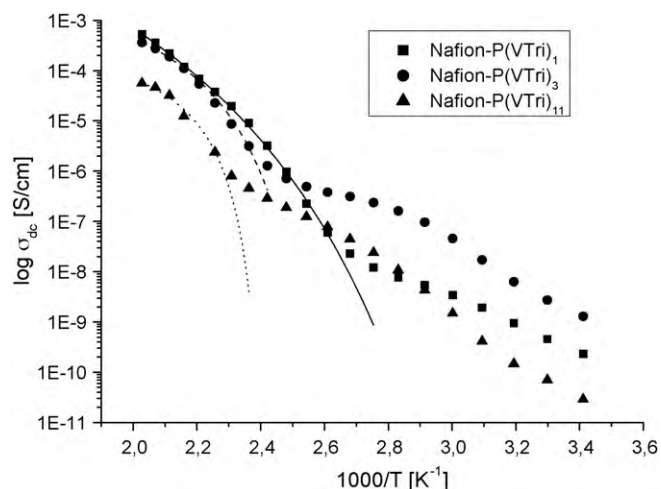
Fig. 11. Typical cyclic voltammograms of PVTri with baseline; $C = 5 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} TEABF$_4$-CH$_3$CN solution at 25 °C.

Fig. 13. Proton conductivity versus reciprocal temperature for anhydrous Nafion–PVTri blend electrolytes.

Table 2
Maximum anhydrous proton conductivities and VTF parameters of the blend membranes.

Sample	Max. conductivity (S cm^{-1})	Log σ_0	T_0 (K)	E_v (eV)
Nafion–P(VTri)$_1$	5.3×10^{-4} at 220 °C	0.58	276	0.166
Nafion–P(VTri)$_3$	3.6×10^{-4} at 220 °C	−1.78	368	0.041
Nafion–P(VTri)$_{11}$	3.6×10^{-5} at 220 °C	−3.21	406	0.018

(3));

$$\log \sigma = \log \sigma_0 - \frac{E_v}{[k(T - T_0)]} \tag{3}$$

where σ_0 is the conductivity at infinite temperature, E_v is the Vogel activation energy and T_0 the Vogel temperature. High accuracy of the VTF parameters (Table 2) proves the contribution of segmental relaxations to the conductivity.

Normally, perfluorosulfonic acid membranes have sulfonic acid groups and hydration is the critical factor to maintain its conductivity. Previously it was reported that the conductivity increased linearly with water content and maximum conductivity of 8.7×10^{-2} S cm^{-1} was reached at 100% relative humidity [29]. The conductivity dropped over 100 °C due to loss of absorbed humidity. Several attempts have been made to improve the conductivity performance of the hydrated perfluorosulfonic acid systems at higher temperatures [30]. An important method was the replacement of water with another proton solvent that has an ability to conduct proton in the anhydrous state. In this context, Nafion membranes were swollen with non-aqueous proton solvents such as triazole, amino triazole, tetrazole, imidazole, imidazole-imidazolium salt solutions [14,31]. These anhydrous polymer membranes exhibited a conductivity of around 10^{-3} S cm^{-1}.

It was reported that water-free polymer systems enable the formation of protonic defects and provide strongly labile proton donor acceptor functions. Heterocycles such as imidazole and pyrazole were promising in that respect where their basic nitrogen sites act as strong proton acceptors with respect to the acid group in the polymer, thus forming proton charge carriers [10]. Also 1H-1,2,4-Triazole (Tri), 3-amino-1,2,4-triazole (ATri) and 5-aminotetrazole (ATet) are highly thermally stable and low volatile heterocyclic protogenic solvents compared to imidazole ($T_{m, imidazole}$ = 90 °C). In our previous work, Nafion–Tri, Nafion–ATri and Nafion–ATet were produced by filling of the hydrophilic channels of the host matrix [14]. At maximum azole contents, the respective proton conductivities

Fig. 12. Cole–Cole plot of Nafion–P(VTri)$_1$ at 160 °C (a) and at 220 °C (b).

temperatures ($T > 100$ °C). The conductivity decrease at higher PVTri containing samples may be attributed to threshold composition of the guest polymer. The curved DC conductivity isotherm can be described by Vogel–Tamman–Fulcher (VTF, Eq.

of the anhydrous blend membranes, Nafion–ATet, Nafion–Tri and Nafion–ATri were 1.6×10^{-4}, 7.7×10^{-4} and 1.1×10^{-3} S cm^{-1} at $180\,^\circ$C.

In the context of polymer–polymer systems, different Nafion/PBI blends were reported by earlier groups [15,16]. The conductivity of these systems depends on the water content as well as PBI content. Also the methanol permeability as well as conductivity performance of these systems was improved compared to Nafion.

The proton conductivity of Nafion–P(VTri)$_n$ systems was studied completely in anhydrous state. The proton conductivity of Nafion–P(VTri)$_1$ is 5.3×10^{-4} S cm^{-1} at $220\,^\circ$C under completely anhydrous state. Similar to Nafion/PBI systems it decreased with PVTri content [16]. In the blended system, proton conductivity may occur over the triazole units which, aggregate to form dynamical hydrogen bonded chains, supporting long range high proton transport. Proton conductivities of blend membranes exceeded 10^{-3} S cm^{-1} in the 50% hydrated state at room temperature.

These results showed that Nafion–PVTri system has improved mechanical, thermal as well as electrochemical stability and also lower methanol permeability that can be suggested for high temperature PEMFC applications.

4. Conclusions

In this work, novel high temperature stable proton conducting polymer blend membranes based on Nafion–P(VTri)$_n$ system were investigated. The membranes were prepared successfully solution casting which leaded to controlled impregnation of the PVTri into Nafion. The materials showed high chemical and thermal stability, i.e., Nafion–P(VTri)$_n$ systems decompose well above $300\,^\circ$C. Calorimetric studies illustrated that the blended systems have no first order or glass transition up to $200\,^\circ$C. SEM results demonstrated that Nafion–P(VTri)$_n$ membranes are homogeneous irrespective to composition. From the FT-IR studies, it was found that protons are dissociated from the acidic groups and protonated azole units of the polymer, leading to hydrogen bonding network formation. Compared to Nafion 112, the blend membrane Nafion–P(VTri)$_1$ has lower water uptake that proves the polymer complex formation. The swelling character of the membranes increased with the fraction of PVTri in Nafion. Methanol permeability experiments demonstrated that the anhydrous blend membranes have lower methanol permeability compared to pristine Nafion112. Electrochemical stability of PVTri was confirmed by cyclic voltammetry. In the anhydrous state, Nafion–P(VTri)$_1$ system has the highest proton conductivity of 5.3×10^{-4} S cm^{-1} at $220\,^\circ$C. After humidification the conductivity of the samples increased about three orders of magnitude at the corresponding temperatures.

These results demonstrated that the insertion of PVTri into hydrophilic channels of Nafion resulted in the production of electrochemically, thermally and mechanically stable membranes that can be suggested for application as polymer electrolyte membrane for direct methanol fuel cells.

Acknowledgement

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