

Synthesis and characterization of composite membranes based on α -zirconium phosphate and silicotungstic acid

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Abstract

The functional properties of the composite membrane generated from polyvinyl alcohol, zirconium phosphate and silicotungstic acid are described. The fabricated membranes were characterized by using FT-IR, XRD, TGA, DSC and SEM techniques. These fabricated membranes showed reduced methanol cross over (for possible application in DMFC) relative to that of Nafion[®] 115. A maximum proton conductivity of 10^{-2} S cm⁻¹ at 60% RH was attained with 30 wt% STA incorporated composite membrane. This is however lower than that observed for Nafion[®] 115 at 100% RH.

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1. Introduction

Fuel cells are emerging as an alternate energy source for mobile and stationary applications. The successful performance of a fuel cell depends critically on the role of the membranes. Though Nafion[®] (a perfluorosulfonated polymer marketed by Ms. Du Pont) has been identified as the preferred membrane for PEM fuel cells, various attempts have been made to develop alternate, adaptable and acceptable class of membranes. Nafion[®] membranes currently employed in hydrogen oxygen fuel cells are not appropriate for use in DMFC since Nafion[®] exhibits reduced conductivity at low humidity condition and/or at elevated temperatures. In addition considerable fuel crossover takes place. Nafion[®] based membranes are unstable at temperatures higher than 353 K. These limitations have prompted search for alternate membranes. Various approaches have been made like: (i) modifying perfluorosulfonic acid (PFSA) membranes to improve their water retention properties at temperatures above 373 K by crosslinking [1–5], or by forming composites with hygroscopic oxides, MO₂ (M = Zr, Si, Ti) [6,7] or with inorganic proton conductors [8–13], (ii) by selecting other non

fluorinated polymer electrolytes such as sulfonated polyetherketones [14], and sulfonated polyetheretherketones [15,16], sulfonated poly arylene ethersulfone (PES) [17], basic polymers such as, poly(4-vinylpyridine) [18], polybenzimidazole [18]. However, sulfonation of these polymers are not simple, and will demand exacting experimental conditions [19] and (iii) designing inorganic organic composite membranes [20–28]. This has attracted attention, because such composites may show controllable physical properties, such as thermal, electrical and mechanical behavior, by combining the properties of both organic polymers and inorganic compounds (solid inorganic proton conductors). Solid inorganic proton conductors like zirconium phosphates, heteropolyacids (HPAs), metal hydrogen sulfates have dual role of being both hydrophilic and proton conducting. However, HPAs are generally water-soluble. Consequently, a major research objective is to fix the HPAs in stable structure by forming composites [25,29–31] which can maintain their high proton conductivity. Composite matrix reduces the leaching of HPA. The scope of the present study is to investigate a composite membrane made of polyvinyl alcohol (PVA) and zirconium phosphate (α -ZrP) with silicotungstic acid (SWA) as an active moiety. Water insoluble zirconium phosphate was added to suppress crack formation due to the shrinkage caused during drying. It also contributes to protonic conduction through the proton of phosphate moiety and crystalline water thereby

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reducing the humidity dependence on conductivity. The driving force for this attempt is to design newer class of membranes, which may not demand the exacting experimental conditions and critical management of chemical environments that are necessary for the synthesis of membranes like Nafion[®] and other sulfonated polymers.

2. Experimental

2.1. Materials and membranes preparation

Polyvinyl alcohol (PVA; MW: 125,000), silicotungstic acid (SWA) were obtained from SRL chemicals, orthophosphoric acid (H₃PO₄) was obtained from the E-Merck and zirconium oxychloride (ZrOCl₂·8H₂O) was obtained from Loba Chemie and were used as received.

2.1.1. Preparation of zirconium phosphate

Zirconium phosphate is prepared by taking 1 M aqueous solution of ZrOCl₂·8 H₂O and it is slowly added to a 10 times excess of 1 M H₃PO₄. The precipitate was washed several times with deionized water, dried 2 h at 368 K and stored at 100% RH and room temperature.

2.1.2. Synthesis of PVA–ZrP–SWA composite membranes

The composite membranes were prepared by sol–gel process. A 10% solution of PVA in water was made by constant stirring at 343 K and to that zirconium phosphate (10 wt%) and silicotungstic acid (10, 20 and 30 wt%) was added and the resultant mixture was refluxed at 343 K for 8 h, to obtain a clear viscous solution. The resulting viscous solution was gelled for 2 days. The film was cast on a clean glass plate with the desired thickness and dried at room temperature.

2.2. Structural characterization

The FT-IR (Perkin-Elmer) spectra for the samples were recorded in the range 400–4000 cm⁻¹ at room temperature. X-ray diffraction patterns were collected with a Rigaku D/max 2400 powder diffractometer using a Cu K α radiation. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA (Delta Series TGA 7) instrument at a heating rate of 20 K min⁻¹ in air. The differential scanning calorimetry (DSC) measurements were performed on the dried samples, in the range of temperature between 323 and 823 K using a Perkin-Elmer DSC-7 instrument. Scanning electron microscope (FEI, Model: Quanta 200) was used to observe the microstructures of the dried membranes.

2.3. Water uptake

The water uptake of the composite membrane was determined by measuring the change in the weight after the hydration. The membrane was first immersed in deionized water for 2 h. Then the membrane was weighed quickly after removing the surface attached water to determine the weight of wetted membrane (W_{wet}). The weight of the dry membrane (W_{dry}) was determined

after drying. The percentage of water uptake was calculated by using the following equation:

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100.$$

2.4. Swelling

The surface swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 2 h. The swelling ratio was calculated by the following equation:

$$\text{swelling (\%)} = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100$$

where, A_{dry} and A_{wet} are the area of dry and wet samples, respectively.

2.5. Ion-exchange capacity (IEC)

The ion exchange capacity of the membranes was determined through an acid–base titration. The dry composite membrane was immersed in 50 ml of 1 M sodium chloride aqueous solution for 24 h in order to extract all protons from the membrane. After taking out the membrane, electrolyte solution was titrated with 5 mM sodium hydroxide solution using phenolphthalein as an indicator. The ion exchange capacity (IEC) was calculated using the following equation:

$$\text{IEC} = \frac{V \times M}{W_{\text{dry}}}$$

where IEC is the ion exchange capacity (mequiv. g⁻¹), V the added titrant volume at the equivalent point (ml), M the molar concentration of the titrant and W_{dry} is the dry mass of the sample (g).

2.6. Proton conductivity

Proton conductivity was measured by an ac impedance technique (Autolab, PGSTAT 30) using two probe method, where the ac frequency was scanned from 1 MHz to 10 Hz at voltage amplitude of 5 mV. The proton conductivity (σ) of the samples in the longitudinal direction was calculated from the impedance data, using the relationship $\sigma = d/Rt$, where d is the distance between the electrodes, t and l are the thickness and width of the films, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis, where Re refers to ‘Real’ in the complex impedance plane. Prior to the proton conductivity measurements, membranes were immersed in deionised water for 24 h to attain hydration equilibrium. Fully hydrated membranes were sandwiched in a Teflon[®] conductivity cell equipped with Pt foil contacts and the impedance was measured by placing the cell in a temperature-controlled chamber under a temperature range of 303–373 K. Constant humidity was maintained at 60% RH by using saturated sodium nitrite and it was sensed by a

hygrometer which was calibrated prior to the experiments. The experiments were repeated three times to check the reproducibility. The variation in the results was found to be less than 2%.

2.7. Methanol crossover

Cyclic voltammetric technique was used to estimate the amount of crossed over methanol. For the experiment, a two-compartment glass cell with the membrane separating the two compartments was used. Prior to the measurements, membranes were immersed in deionised water for 24 h to attain hydration equilibrium. Platinum foil with a geometric surface area of 2 cm² and smooth platinum electrode were used as working and counter electrode, and Ag/AgCl (saturated KCl) electrode as the reference. The working electrode was immersed in one compartment considered as cathode and counter and reference electrode was immersed in the second compartment considered as anode. The cell was connected to BAS Epsilon potentiostat. A blank electrolyte of 50 ml of 0.5 M H₂SO₄ was first taken in either compartment of the cell and CV scanning was performed prior to the permeability test. The permeability was studied by introducing methanol of known concentration in 0.5 M H₂SO₄ to one compartment of the cell and analyzing the other compartment for its permeability. The permeability test was performed at room temperature for 1 M initial methanol concentration at the anode compartment and cyclic voltammograms was recorded between 0.2 and 1 V and from the response the concentration of methanol in the cathode side was determined. The concentration of crossed methanol was determined from the calibration

curve which was obtained as described by Ling and Savadogo [32]. The experiments were repeated three times to check the reproducibility. The variation in the results was found to be less than 2%.

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra obtained for the membrane are given in Fig. 1. The spectrum of a typical membrane reveals the characteristic bands of PVA, α -ZrP and salt of SWA. The FT-IR spectrum of hybrid membranes showed bands at 970, 917, 850 and 790 cm⁻¹, which agree with those reported in literature [33,34] for this silicotungstic acid. The bands around 3275 and 2940 cm⁻¹ represent O–H stretching and –CH₂ stretching; the band around 1440 cm⁻¹ is for –CH₃ bending, all these bands are characteristics of PVA. The bands around 506 and 1080 cm⁻¹ are due to Zr–O and P–O₄ asymmetric stretching which are characteristics of ZrP [35]. The positions of vibration modes of all types of M–O bonds are strongly influenced by interaction of silicotungstic with the polymer and zirconium phosphate. The band of W–O_b–W (O_b: bridged oxygen and O_t: terminal oxygen) has a blue shift from 758 to around 790 cm⁻¹ and W–O_t bond of SWA in the composite is red shifted from 972 to 918 cm⁻¹. This is due to the columbic interaction between the hydroxyl groups of the polyvinyl alcohol and silicotungstic acid. The main bands are assigned and tabulated separately for composite membranes in Table 1.

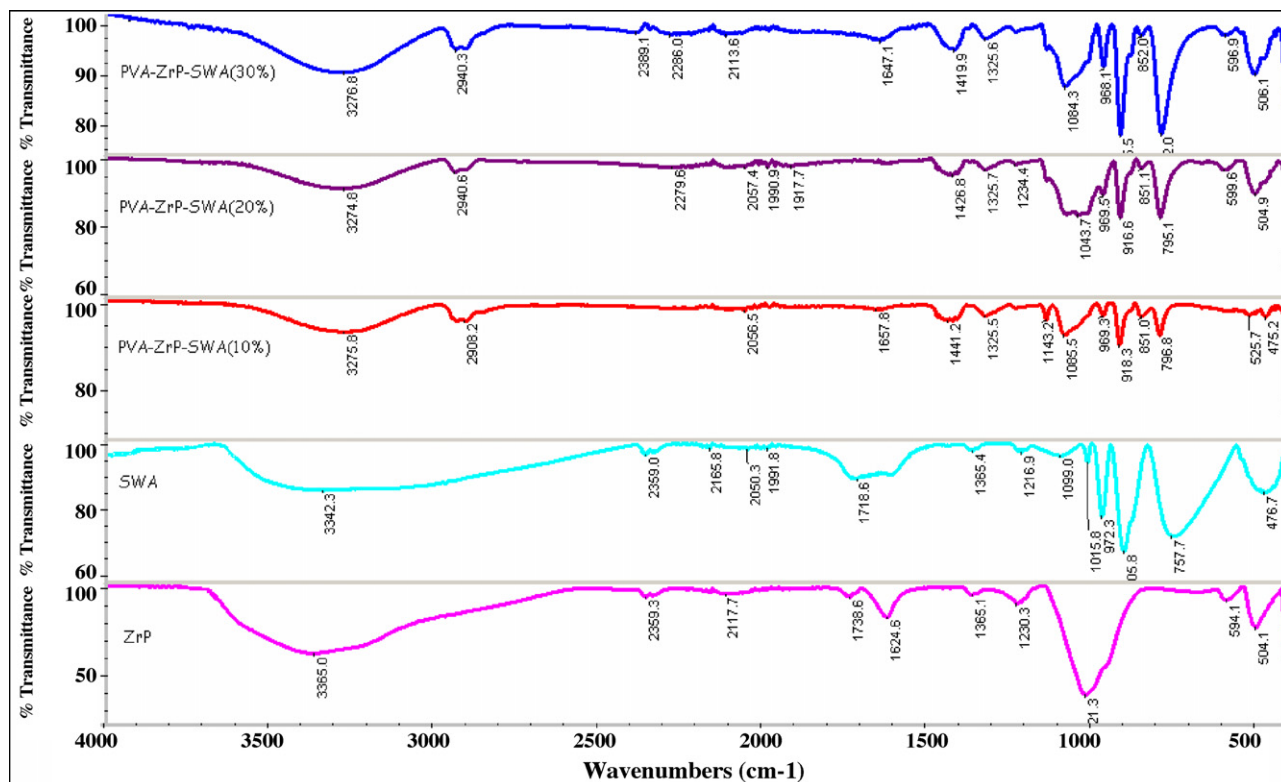


Fig. 1. FT-IR spectra of composite membranes and its components.

Table 1
Assignments of main absorption bands for composite membranes and its components

Composite membranes		α -ZrP		SWA		PVA	
Vibration frequency (cm^{-1})	Bond assignment	Vibration frequency (cm^{-1})	Bond assignment	Vibration frequency (cm^{-1})	Bond assignment	Vibration frequency (cm^{-1})	Bond assignment
506	$\nu_{\text{as}}(\text{Zr-O})$	504	$\nu_{\text{as}}(\text{Zr-O})$	758	$\nu(\text{W-O}_b\text{-W})$	1420	$\nu(\text{CH}_3)$
600	$\delta_{\text{out}}(\text{POH})$	594	$\delta_{\text{out}}(\text{POH})$	906	$\nu(\text{Si-O})$	2900	$\nu(\text{CH}_2)$
790	$\nu(\text{W-O}_b\text{-W})$	1021	$\nu_{\text{as}}(\text{PO}_4)$	972	$\nu_{\text{as}}(\text{W-O}_t)$	3260	$\nu(\text{OH})$
917	W-O_t	1624	$\delta_{\text{as}}(\text{OH})$				
970	$\nu_{\text{as}}(\text{W=O}_t)$	2117	$\nu(\text{POH})$				
1080	$\nu_{\text{as}}(\text{PO}_4)$	2359	$\nu(\text{POH})$				
1440	$\nu(\text{CH}_3)$	3365	$\nu_{\text{as}}(\text{OH})$				

3.2. XRD

Fig. 2 shows the XRD profiles obtained for composite membranes. X-ray investigation was made to provide information about the structural changes induced by the presence α -ZrP and SWA. For comparison the XRD patterns for PVA and α -ZrP are also given. The peak occurring at $2\theta = 20^\circ$ corresponds to the (101) plane of PVA in all composite membranes [36]. Broad peaks of the α -ZrP powder indicate that α -ZrP is in the amorphous state. No diffraction peaks characteristic of SWA appears in the spectra containing 10, 20 and 30% of SWA. This is a consequence of finely dispersed SWA in the polymer matrix and the composite behaves as X-ray amorphous. Broad peaks also indicate the conformation of complete homogeneity and compatibility among the components of the membrane.

3.3. Thermal analysis

The TGA obtained for the membranes are shown in Fig. 3. Three degradation stages are seen. The first weight loss occurs around 373 K, due to loss of absorbed water molecules. The second weight loss in the temperature region 460–573 K is due to decomposition of polyvinyl alcohol. The third weight loss is due to decomposition of silicotungstic acid to respective metal

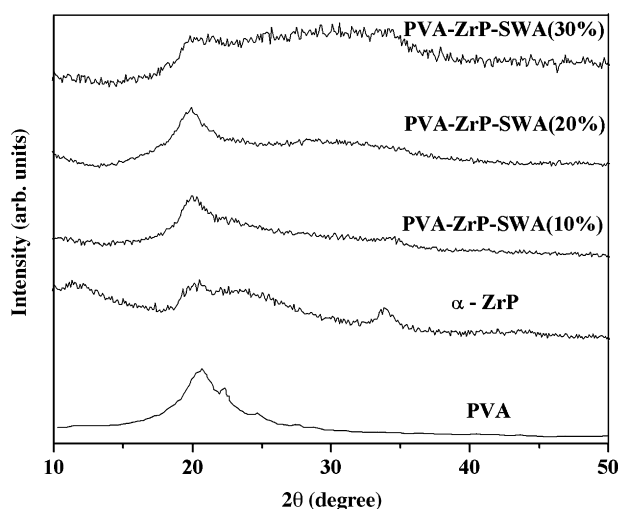


Fig. 2. Cu K α XRD patterns of composite membranes and its components for comparison.

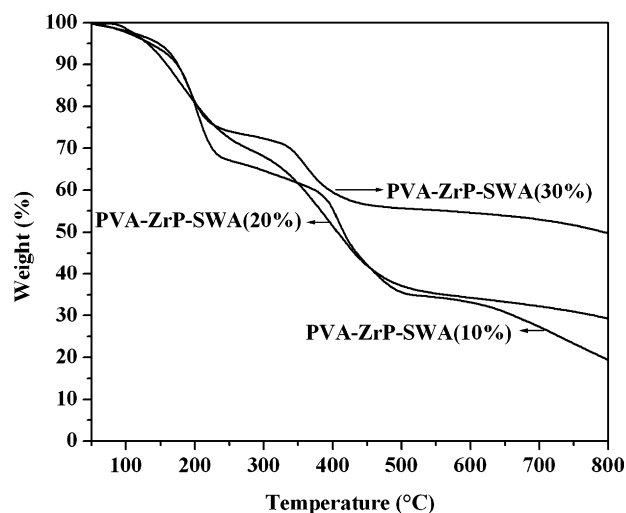


Fig. 3. TGA analysis of composite membranes in a temperature range from 50 to 800 °C.

oxides. The DSC thermograms of the composite membranes are presented in Fig. 4. PVA is partially crystalline polymer exhibiting both the glass transition temperature, T_g (characteristic of amorphous phase) and melting isotherm, T_m (characteristic of

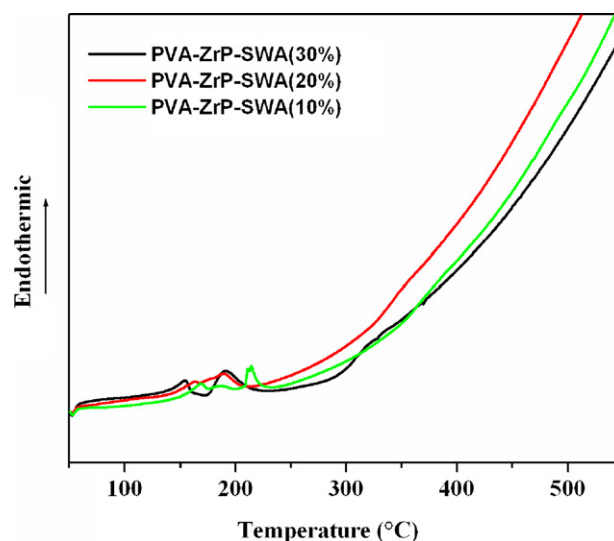


Fig. 4. DSC thermograms of composite membranes with different contents of silicotungstic acid.

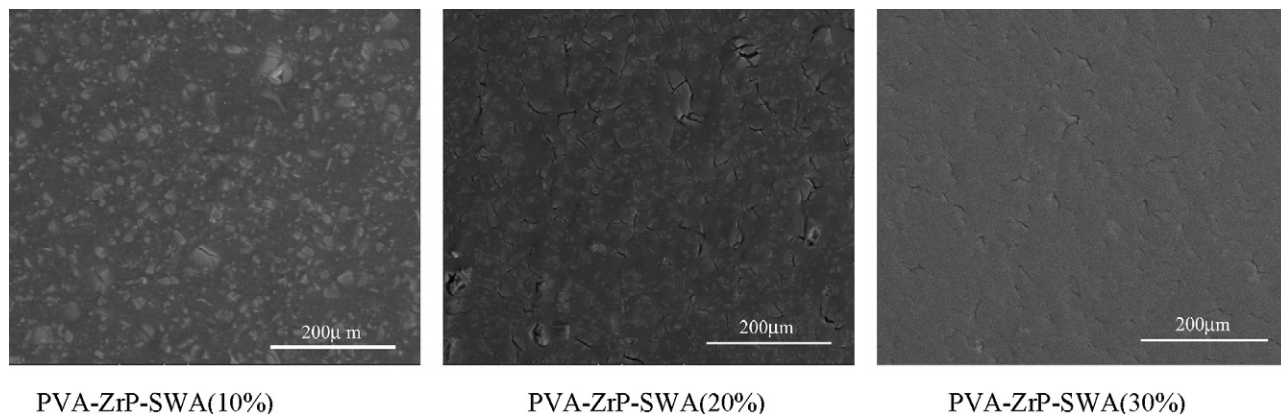


Fig. 5. Scanning electron micrographs of composite membranes.

crystalline phase). For pure PVA the glass transition temperature is around 363 K and melting temperature is around 489 K [37]. T_g of composite membranes are observed around 398 K which is much higher than that of pure PVA. The increased T_g due to the presence of α -ZrP indicates the increase in thermal stability of the composite membranes. The reason for the increase in thermal stability of composite membranes probably is due to the formation of hydrogen bonds or the condensation reaction between the residual $-OH$ on the α -ZrP and the $-OH$ on PVA. With increasing SWA content T_g of the composite membranes decreases. It can be attributed to softening of the complexation due to the plasticizing effect of SWA on the polymer structure, which is beneficial for the proton transport in the membrane. The second endothermic peak corresponds to the melting of the crystalline phases of composite membranes. For pure PVA the endothermic peak at 493 K is associated with the melting point of the polymer [37]. The melting temperature, T_m , was taken as the maximum of the transition, whereas the heat of fusion, H_f , which increases with the crystallinity of the polymer, was calculated as the integrated area of the transition peak. The melting point is reduced to 483, 464 and 462 K for 10%, 20% and 30% SWA containing composite membranes respectively; the heat of fusion, H_f , is around 109, 73 and 45 J g⁻¹ respectively. The interaction between the polymer and inorganic components breaks the preformed crystals to render the polymer in the amorphous phase to some extent, which favors the improvement of conductivity. The broad endothermic peak until around 250 °C can also be attributed to the dehydration of crystalline water.

3.4. SEM

Surface morphology of the dried membrane was investigated using SEM. Fig. 5 shows the scanning electron micrographs of 10, 20 and 30 wt% SWA acid substituted composite membranes. The distribution of inorganic particles is relatively uniform in the organic matrix. Membranes are compact with low degree of porosity. In the case membranes with 30 wt% of SWA, no phase separation was observed, suggesting that the synthesized films were homogeneous in nature and hence formed dense membrane.

3.5. Water uptake, swelling and IEC

The presence of water in the membrane greatly influences the basic properties of the membrane. The water uptake and ion exchange capacity (IEC) play important roles in membrane conductivity. Proton conductivity of the membrane will increase with increasing water uptake and IEC because of the increase in the mobility of ions. The data on water uptake, extent of swelling and IEC data for the membranes are given in Table 2. At room temperature the water absorption, extent of swelling and IEC increases with increase in the content of SWA for membranes of 250 μ m thickness.

3.6. Proton conductivity

The temperature dependence of the conductivity of the membrane for different wt% of SWA is shown in Fig. 6. At 60% of relative humidity, the protonic conductivity of the composite membranes was in the range of 10⁻³ S cm⁻¹. The proton conductivity increased with increasing SWA content. This trend was the same as that observed for water uptake and IEC. Conductivity increased with temperature and it attains maximum at 333 K and remains constant up to 353 K. For the composite membrane containing 30% SWA exhibited conductivity value of 10⁻² S cm⁻¹ in the temperature range of 333–353 K. After 353 K conductivity drops due to the evaporation of adsorbed water. Though there is a decrease in conductivity at temperature above 353 K the order of magnitude remains the same. For comparison, the corresponding data for Nafion® 115 measured at 100% relative humidity is included in Fig. 6.

In the fabricated membrane, ZrP and SWA are the active proton conducting moieties. The proton conductivity of the com-

Table 2
Water uptake, swelling and IEC values for different composite membranes with a 250 μ m thickness

Membrane	Water uptake (%)	Swelling (%)	IEC (mequiv. g ⁻¹)
PVA-ZrP-SWA (10%)	204	90	0.902
PVA-ZrP-SWA (20%)	388	170	0.958
PVA-ZrP-SWA (30%)	482	230	1.07

Table 3

Proton conductivity (σ) and activation energy (E_a) for composite membranes and its components

Proton conductor	Proton conductivity ($S\text{ cm}^{-1}$)	Conditions	Activation energy (kJ mol^{-1})	Reference
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	10^{-5} to 10^{-6}	293 K, 90% RH	48.2	[38]
$\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$	10^{-2}	298 K, 97% RH	38.5	[39]
Polyvinyl alcohol	10^{-6}	312 K	–	[40]
PVA–ZrP–SWA (10%)	3×10^{-3}	333 K, 60% RH	6	Obtained from our measurements
PVA–ZrP–SWA (20%)	4×10^{-3}	333 K, 60% RH	4.8	
PVA–ZrP–SWA (30%)	1×10^{-2}	333 K, 60% RH	3	

ponents of the composite membrane is tabulated and compared to the fabricated membranes (Table 3). All the three components contribute to proton conductivity. In the fabricated composite membranes by combining both organic component PVA and inorganic components ZrP and SWA, the conductivity of the system improved. The activation energy (E_a) for conduction in the fabricated membranes is also affected by forming composite. The E_a , decreased compared to its components (Table 3). For membranes containing 10, 20 and 30 wt% of SWA the E_a values are 6, 4.8 and 3 kJ mol^{-1} , respectively. This trend is due to the increase in water content with increase in SWA.

3.7. Methanol crossover

Concentration of crossed over methanol with time was plotted for all composite membranes and it is compared with that of Nafion[®] 115 in Fig. 7. Initially for all composite membranes, the concentration of crossed over methanol increased with time and after 90 min it reached a steady value. There is no appreciable increase in crossover up to 180 min. In the case of Nafion[®] 115, the concentration of crossed over methanol increased linearly with time. Compared to Nafion[®] 115, methanol crossover was reduced by a factor of 2 for 10 wt% SWA composite membrane. As SWA percentage increased crossover decreased tremendously. In the case of 30 wt% SWA substituted composite membrane methanol crossover was a magnitude less than that of Nafion[®] 115. Reduced crossover in composite membranes

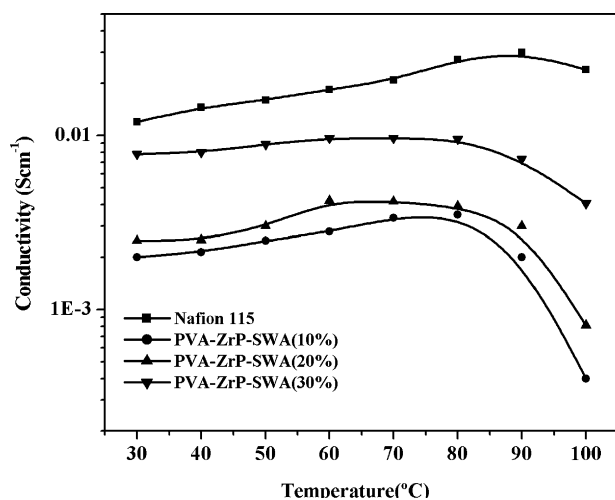


Fig. 6. Proton conductivity at 60% RH as a function of temperature for PVA–ZrP–SWA (10%), PVA–ZrP–SWA (20%), PVA–ZrP–SWA (30%) and Nafion[®] 115 (at 100% RH).

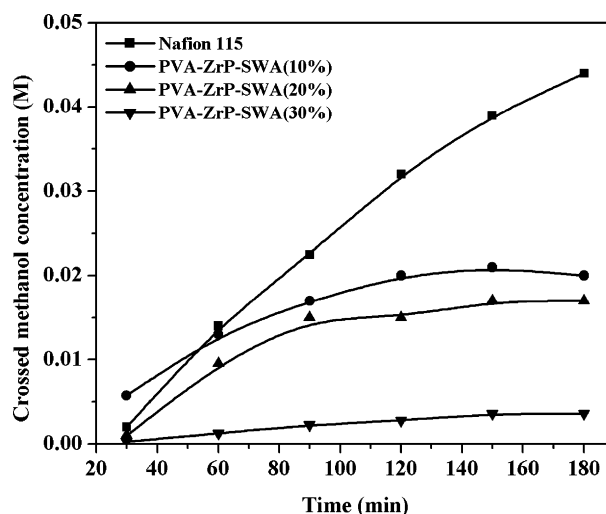


Fig. 7. Concentration of crossed methanol as a function of crossover time.

is due to the hydrophilic nature of the fabricated membrane which is capable of retaining methanol. Whereas, in the case of Nafion[®] 115 the hydrophobic nature of the polymer allows methanol crossover to a greater extent. As shown in Fig. 8 the methanol permeability for all membranes was less compared to that of Nafion[®] 115. Compared to Nafion[®] 115, PVA–ZrP–SWA composite membranes show strong resistance to methanol permeability at the expense of proton conductivity. This clearly indicates that methanol crossover can significantly be reduced using PVA–ZrP–SWA composite membrane in DMFC.

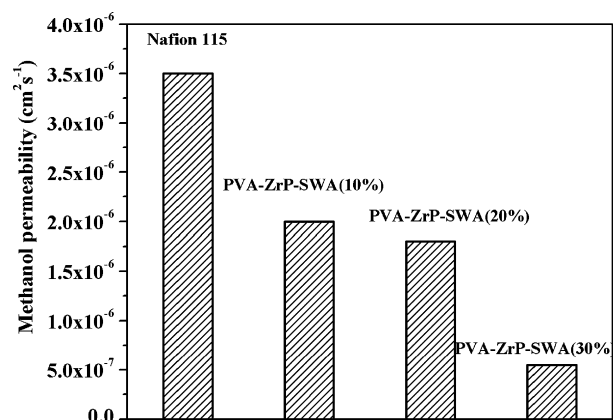


Fig. 8. Methanol permeability of composite membranes compared with Nafion[®] 115.

4. Conclusion

Composite membranes with polyvinyl alcohol as organic matrix and zirconium phosphate and silicotungstic acid as inorganic components were prepared by a simple method. Fabricated membrane was characterized regarding water uptake, swelling, IEC, proton conductivity and for methanol crossover. Water uptake, IEC and proton conductivity increased with silicotungstic acid content. These composite membranes exhibited reduced methanol crossover compared to Nafion® 115. Though they exhibit little lower proton conductivity it appears as promising materials due to its reduced methanol crossover.

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References

- [1] B. Bae, B.H. Chun, H.Y. Ha, I.H. Oh, I.-H. Kim, Preparation and characterization of plasma treated PP composite electrolyte membranes, *J. Membr. Sci.* 202 (2002) 245.
- [2] J. Shim, H.Y. Ha, H.S.A. Hong, I.H. Oh, Characteristics of the Nafion® ionomer-impregnated composite membrane for polymer electrolyte fuel cells, *J. Power Sources* 109 (2002) 412.
- [3] S. Haufe, U. Stimming, Proton conducting membranes based on electrolyte filled microporous matrices, *J. Membr. Sci.* 185 (2001) 95.
- [4] K.M. Nouel, P.S. Fedkiw, Nafion®-based composite polymer electrolyte membranes, *Electrochim. Acta* 43 (1998) 2381.
- [5] W. Liu, K. Ruth, G. Rusch, Membrane durability in PEM fuel cells, *J. New Mater. Electrochem. Syst.* 4 (2001) 227.
- [6] W. Apichatachutapan, R.B. Moore, K.A. Mauritz, Asymmetric, [Nafion®]/[zirconium oxide] compositemembranes via in-situ sol–gel chemistry, *J. Appl. Polym. Sci.* 62 (1996) 417.
- [7] P.L. Shao, K.A. Mauritz, R.B. Moore, {Perfluorosulfonate ionomer}/[mixed inorganic oxide] nanocomposites via polymer-in situ sol–gel chemistry, *Chem. Mater.* 7 (1995) 192.
- [8] C. Yang, S. Srinivasan, A.S. Arico, P. Creti, V. Baglio, V. Antonucci, Composite Nafion® zirconium phosphate membranes for direct methanol fuel cell operation at high temperature, *Electrochem. Solid-State Lett.* 4 (2001) A31.
- [9] F. Bauer, M.W. Porada, Microstructural characterization of Zr-phosphate–Nafion® membranes for direct methanol fuel cell (DMFC) applications, *J. Membr. Sci.* 233 (2004) 141.
- [10] Y.T. Kim, M.K. Song, K.H. Kim, S.B. Park, S.K. Min, H.W. Rhee, Nafion/ZrSPP composite membrane for high temperature operation of PEMFCs, *Electrochim. Acta* 50 (2005) 645.
- [11] V. Ramani, H.R. Kunz, J.M. Fenton, Stabilized heteropolyacid/Nafion® composite membranes for elevated temperature/low relative humidity PEFC operation, *Electrochim. Acta* 50 (2005) 1181.
- [12] Z.-G. Shao, H. Xu, M. Li, I.-M. Hsing, Composite Nafion–inorganic oxides membrane doped with heteropolyacids for high temperature operation of proton exchange membrane fuel cell, *Solid State Ionics* 177 (2006) 779.
- [13] P. Staiti, A.S. Arico, V. Baglio, F. Lufano, E. Passalacqua, V. Antonucci, Composite Nafion–silica membranes doped with heteropolyacids for application in direct methanol fuel cells, *Solid State Ionics* 145 (2001) 101.
- [14] C. Bailly, D.J. Williams, F.E. Karasz, W.J. MacKnight, The sodium salts of sulfonated poly(aryl ether-ether-ketone) (PEEK): preparation and characterization, *Polymer* 28 (1987) 1009.
- [15] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, Casting solvent interactions with sulfonated poly(ether ether ketone) during proton exchange membrane fabrication, *J. Membr. Sci.* 219 (2003) 113.
- [16] S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, M. Guiver, Properties of SPEEK based PEMs for fuel cell application, *Catal. Today* 82 (2003) 213.
- [17] R. Nolte, K. Ledjeff, M. Bauer, R. Mülhaupt, Partially sulfonated poly(arylene ether sulfone)—A versatile proton conducting membrane material for modern energy conversion technologies, *J. Membr. Sci.* 83 (1993) 211.
- [18] L. Jorissen, V. Gogel, J. Kerres, J. Garche, New membranes for direct methanol fuel cells, *J. Power Sources* 105 (2002) 267.
- [19] M. Yoshikawa, K. Tsubouchi, M.D. Guiver, G.P. Robertson, Modified poly-sulfone membranes. III. Pervaporation separation of benzene–cyclohexane mixtures through carboxylated polysulfone membranes, *J. Appl. Polym. Sci.* 74 (1999) 407.
- [20] T. Tezuka, K. Tadanaga, A. Matsuda, A. Hayashi, M. Tatsumisago, Utilization of glass papers as a support for proton conducting inorganic–organic compositemembranes from 3-glycidoxypropyltrimethoxysilane, tetraalkoxysilane and orthophosphoric acid, *Solid State Ionics* 176 (2005) 3001.
- [21] S. Li, Z. Zhou, M. Liu, W. Li, J. Ukai, K. Hase, M. Nakanishi, Synthesis and properties of imidazole-grafted compositeinorganic–organic polymer membranes, *Electrochim. Acta* 51 (2006) 1351.
- [22] P.G. Romero, J.A. Asensio, S. Borrós, Composite proton-conducting membranes for polymer electrolyte fuel cells: phosphomolybdic acid doped poly(2,5-benzimidazole)—(ABPBI-H₃PMO₁₂O₄₀), *Electrochim. Acta* 50 (2005) 4715.
- [23] D.R. Vernon, F. Meng, S.F. Dec, D.L. Williamson, J.A. Turner, A.M. Herring, Synthesis, characterization, and conductivity measurements of compositemembranes containing a mono-lacunary heteropolyacid for PEM fuel cell applications, *J. Power Sources* 139 (2005) 141.
- [24] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, Preparation and characterization of crosslinked PVA/SiO₂ compositemembranes containing sulfonic acid groups for direct methanol fuel cell applications, *J. Membr. Sci.* 240 (2004) 37.
- [25] S. Shanmugam, B. Viswanathan, T.K. Varadarajan, Synthesis and characterization of silicotungstic acid based organic–inorganic nanocomposite membrane, *J. Membr. Sci.* 275 (2006) 105.
- [26] S. Panero, P. Fiorenza, M.A. Navarra, J. Romanowska, B. Scrosati, Silica-added composite poly(vinyl alcohol) membranes for fuel cell application, *J. Electrochem. Soc.* 152 (2005) A2400.
- [27] B. Ruffmann, H. Silva, B. Schulte, S.P. Nunes, Organic/inorganic composite membranes for application in DMFC, *Solid State Ionics* 162–163 (2003) 269.
- [28] W. Xu, C. Liu, X. Xue, Y. Su, Y. Lv, W. Xing, T. Lu, New proton exchange membranes based on poly(vinyl alcohol) for DMFCs, *Solid State Ionics* 171 (2004) 121.
- [29] B. Tazi, O. Savadogo, Parameters of PEM fuel cells based on new membranes fabricated from Nafion®, silicotungstic acid and thiophene, *Electrochim. Acta* 45 (2000) 4329.
- [30] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications, *J. Membr. Sci.* 173 (2000) 17.
- [31] C.W. Lin, R. Thangamuthu, P.H. Chang, PWA-doped PEG/SiO₂ proton-conducting compositemembranes for fuel cell applications, *J. Membr. Sci.* 254 (2005) 197.
- [32] J. Ling, O. Savadogo, Comparison of methanol crossover among four types of nafion membranes, *J. Electrochem. Soc.* 151 (2004) A1604.
- [33] T. Okuhara, N. Mizuno, M. Misono, Catalytic chemistry of heteropoly compounds, *Adv. Catal.* 41 (1996) 113.
- [34] C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Franck, Spectres i.r. et Raman d'hétéropolyanions α -XM₁₂O₄₀ⁿ⁻ de structure de type Keggin (X = B^{III}, Si^{IV}, Ge^{IV}, P^V, As^V et M = W^{VI} et Mo^{VI}), *Spectrochim. Acta A* 32 (1976) 587.
- [35] S.E. Horsley, D.V. Nowell, D.T. Stewart, The infrared and Raman spectra of α -zirconium phosphate, *Spectrochim. Acta* 30A (1974) 535.
- [36] C.I. Shao, H.Y. Kim, J. Gong, B. Ding, D.R. Lee, S.J. Park, Fiber mats of PVA/silica composite via electrospinning, *Mater. Lett.* 57 (2003) 1579.

- [37] C.M. Hassan, N.A. Peppas, Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional cross-linking or by freezing/thawing methods, *Adv. Polym. Sci.* 153 (2000) 37.
- [38] G. Alberti, M. Casciola, Layer hydrates, in: P. Colomban (Ed.), *Proton Conductors*, Cambridge University Press, New York, 1992, p. 238.
- [39] K.D. Kreuer, M. Hampele, K. Dolde, A. Rabenau, Proton transport in some heteropolyacidhydrates a single crystal PFG-NMR and conductivity study, *Solid State Ionics* 28–30 (1988) 589.
- [40] S.L. Agrawal, A. Awadhia, DSC and conductivity studies on PVA based proton conducting Gel electrolytes, *Bull. Mater. Sci.* 27 (2004) 523.