Synopsis of

DEVELOPMENT OF HYBRID MEMBRANES FOR APPLICATION IN DIRECT METHANOL FUEL CELLS (DMFC)

A Thesis

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1. INTRODUCTION

Fuel cells are emerging as an alternate energy source for mobile and stationary applications. Among low temperature fuel cells, direct methanol fuel cell (DMFC) is attractive due to its system simplicity and adaptability for a liquid fuel, methanol. The successful performance of a DMFC depends critically on the role of the membranes. Though Nafion® (a perfluorosulphonated polymer marketed by Ms. DuPont) has been identified as the preferred membrane for polymer electrolyte 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 80 ºC. These limitations have prompted the search for alternative 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 (Nouel and Fedkiw, 1998; Haufe and Stimming, 2001), or by forming composites with hygroscopic oxides, MO_2 (M = Zr, Si, Ti) (Shao *et al.,* 1995) or with inorganic proton conductors (Yang *et al.,* 2001; Staiti *et al.,* 2001); (ii) by selecting other non-fluorinated polymer electrolytes such as sulfonated polyetherketones (Bailly *et al.,* 1987), and sulfonated poly(ether ether ketones), sulfonated poly (arylene ether sulfone) (PES) (Nolte *et al.,* 1993), basic polymers such as, poly(4-vinylpyridine), polybenzimidazole (Jorissen *et al.,* 2002). However, sulfonation of these polymers demands exacting experimental conditions; (iii) designing inorganic-organic composite membranes (Ruffmann *et al.,* 2003). 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, heteropoly acids (HPAs), metal hydrogen sulfates have dual role of being both hydrophilic and proton conducting.

Among various hydrophilic polymers, poly(vinyl alcohol) (PVA) exhibits desired characteristic like enhanced chemical stability and acts as an excellent methanol barrier in addition to its film forming capacity, which is essential for an ion-exchange membrane. Since 1986 (Polak *et al.,* 1986), a number of research groups have investigated poly(vinyl alcohol)l based proton conducting membranes. PVA membranes with appropriate swelling properties along with good proton conductivities are needed for use in fuel cells. Increase in water content in the membranes would result in loss of dimensional stability and cause an increase in methanol permeability. Polymer swelling can be reduced by blending, cross-linking or copolymerizing with other suitable polymers, while proton conductivity can be increased by forming hybrids by incorporating proton conductors like heteropoly acids. A major limiting factor to employ heteropoly acids as membrane material for fuel cell application is their extreme solubility in aqueous medium. Forming hybrids with cesium salts of heteropoly acids can surmount this difficulty.

2. OBJECTIVES AND SCOPE OF THE WORK

The driving force for this investigation 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. In literature, there have been various attempts to develop alternate membranes to Nafion® (a monopoly product of Dupont), as indicated in the introduction. However, these attempts have not been very successful due to the fact that it is nearly impossible to design a membrane that will have better ionic conductivity compared to Nafion®, due to its inherent chemical composition, namely, Nafion® holds the utmost electronegative environment possible in a chemical system. Realizing this limitation, it was considered worthwhile to design a membrane which may possess ionic conductivity less than that of Nafion®, but should have at least one property (for fuel cell applications) better than that of Nafion®. Since the fuel crossover from anode to the cathode in a DMFC causes mixed potential at the cathode and hence affects the normally slow reaction of oxygen reduction, it was considered that the membrane development must mainly focus to this aspect of fuel crossover. To focus the issue more precisely the crossover of methanol in case of DMFC is considered as the property of concern.

This investigation therefore focuses on the following aspects of this development:

- To design alternate membrane material processing hydration stability at elevated temperatures, low fuel crossover, with good mechanical, thermal, and oxidative stability and with appreciable proton conductivity. And, of course, all of these objectives must be achieved while maintaining low cost by a simple and controllable fabrication method.

- Formulation and fabrication of alternate membrane material through organic inorganic hybrid formation, by choosing poly(vinyl alcohol) as an organic matrix and heteropoly acid as active component for proton conduction.
- Having chosen a class of advanced membrane material, the following challenges are met with appropriate solutions:
  - i) to fix the additive inorganic component (heteropoly acid) in a stable organic matrix
  - ii) to improve the dimensional stability of PVA based polymer matrix, and
  - iii) to reduce methanol crossover while maintaining appreciable proton conductivity

It is realized that the problem on hand is the most challenging, the solutions sought may not readily yield the final answers but it is believed that they have at least provided some possible (if not appropriate) alternatives to carry the research forward in this field.

3. EXPERIMENTAL METHODOLOGY

The hybrid membranes were prepared by sol-gel process. The fabricated membranes were characterized by using spectroscopic, physicochemical and morphological analyses in addition to relevant electrochemical characterizations. The Fourier transformed infrared (FTIR) spectroscopic measurements (Nicolet 6700 FT-IR interfaced with Omnic software) for the hybrid membranes were made in the wave number range 600–4000 cm^{-1} at room temperature (RT). X-ray diffraction (XRD) patterns were collected with a Rigaku D/max 2400 powder diffractometer using CuK_{α} as a radiation source. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG/DTA (Diamond) instrument at a heating rate of 20 K min^{-1} under air atmosphere. Morphological characteristics of the hybrid membrane materials were examined by using a scanning electron microscope (SEM) (FEI, Model:Quanta 200) to observe the microstructures. Proton conductivity studies of the fabricated membranes were done by employing an alternate current (ac) impedance technique (PARSTAT 2263) using four electrode probe method, in which the ac frequency was scanned from 1 MHz to 1 Hz at an amplitude of 5 mV. 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 303–353 K. Constant relative humidity (RH) was maintained at 50 % RH or 60 % RH by using saturated magnesium nitrate

[$Mg(NO_3)_2$] and sodium nitrite [$NaNO_2$] respectively, and it was sensed by a hygrometer, which was calibrated prior to the experiments. Cyclic voltammetric technique (Bioanalytical Systems (BAS), USA) was used to estimate the amount of crossed-over methanol. For this experiment, a two compartment glass cell was employed by mounting the membrane under examination at the middle by separating the two houses. These experiments were repeated three times to confirm the reproducibility of the results obtained.

4. DESCRIPTION OF THE RESEARCH WORK

4.1. Fabrication and properties of hybrid membranes based on silicotungstic acid, α-zirconium phosphate and poly(vinyl alcohol)

Hybrid membranes made of PVA (*MW*: 125,000, Hydrolysation: 90 %, SRL Chemicals, India) as organic component and HPA as an active component were fabricated. The scope of this part of the study is to investigate hybrid membranes made of poly(vinyl alcohol) (PVA) and zirconium phosphate (α-ZrP) with silicotungstic acid (SWA) as an active moiety. Though HPA are solid electrolytes with good proton conductivity (10^{-2} S cm^{-1}) they cannot be employed as such in fuel cell due to its high solubility (SWA = 222.3 g/100 ml). Formation of composite matrix may lead to prevention of HPA leaching. Hence, our main objective is to fix heteropoly acid in a stable matrix by forming composites with PVA and ZrP, while maintaining their high proton conductivity. Through this attempt, we have mitigated HPA leaching. 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 reducing the humidity dependence on conductivity.

The hybrid membranes with different loading of silicotungstic acid (10, 20 and 30 wt %) were prepared by sol-gel process. The fabricated hybrid membranes were characterized by various physicochemical and morphological studies like FTIR, XRD, TGA and SEM. The positions of vibration modes of all types of W-O bonds are strongly influenced by interaction of silicotungstic acid with the polymer and zirconium phosphate. This is due to the columbic interaction between the hydroxyl groups of the poly(vinyl alcohol) and silicotungstic acid. Thermograms reveal the stability of the hybrid membranes up to 200 ºC. The water uptake and ion exchange capacity (IEC) influences the transport property of the membrane. Proton conductivity of the membrane will increase with increasing water uptake and IEC due to increase in mobility of ions. The data on water uptake, extent of swelling and IEC increased with increase in silicotungstic acid content. This is due to the hygroscopic and proton conducting nature of heteropoly acid.

The temperature dependence of the conductivity of the membrane for different wt % of SWA is shown in Fig. 1. At 60 % of relative humidity, the protonic conductivity of the hybrid 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 60 ºC and remains constant up to 80 ºC. Beyond 80 ºC conductivity drops due to the evaporation of adsorbed water. Though there is a decrease in conductivity at temperature above 80 ºC the order of magnitude remains the same. For comparison, the corresponding data for Nafion® 115 measured at 100 % relative humidity is included in Fig. 1.

As shown in Fig. 2 the methanol permeability for all membranes was less compared to that of Nafion® 115. Compared to Nafion® 115, PVA-ZrP-SWA hybrid membranes show strong resistance to methanol permeability at the expense of proton conductivity. This indicates that methanol cross-over can significantly be reduced using PVA-ZrP-SWA hybrid membrane in DMFC. Reduced crossover in hybrid membranes is due to the hydrophilic nature of the fabricated membrane which is capable of retaining methanol. Where as, in the case of Nafion® 115 the hydrophobic nature of the polymer allows methanol crossover to a greater extent. Though they exhibit little lower proton conductivity it appears as promising materials due to its reduced methanol crossover.

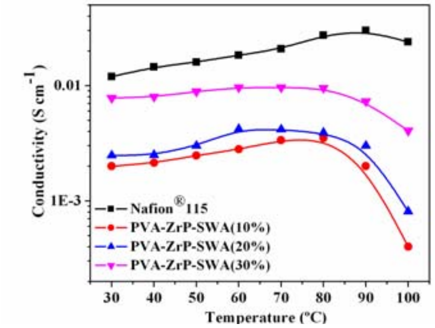

Fig. 1 Proton conductivity at 60% RH as a function of temperature for hybrid membranes and Nafion® 115 (at 100 % RH)

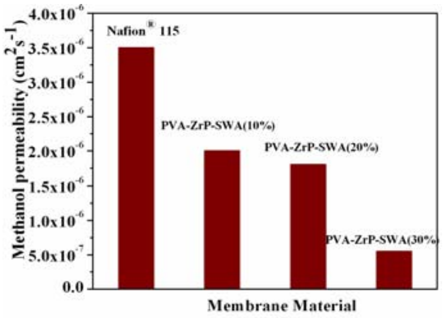

Fig. 2 Methanol permeability of hybrid membranes compared with Nafion® 115

4.2. Fabrication and properties of hybrid membranes based on salts of silicotungstic acid, α-zirconium phosphate and poly(vinyl alcohol)

Heteropoly acids (HPAs) are strong Bronsted acids as well as solid electrolytes. Consequently, a research objective is to fix the HPAs in stable structure by forming hybrids which can maintain their high proton conductivity. Yet another approach in limiting HPAs solubility and leaching is by ion exchanging protons of HPA with larger cations like Cs^+, NH_4^+, Rb^+ and Tl^+ (Ramani *et al.,* 2005). In this work, we employed both these approaches simultaneously by forming composites with poly(vinyl alcohol), zirconium phosphate and cesium salt of silicotungstic acid. The investigation of poly(vinyl alcohol) (PVA) and zirconium phosphate based hybrid membrane with cesium salts of silicotungstic acid as the active component is described.

Fig. 3 shows temperature dependence of the membrane conductivity. At 50 % of relative humidity, the protonic conductivity of the hybrid membranes was in the range of 10^{-3} to 10^{-2} S cm^{-1}. The proton conductivity increased with increasing substitution of proton with cesium. The charge carriers in the acidic salt of silicotungstic acid are increasing leading to increased proton conductivity in PVA-ZrP-Cs_2SWA compared to PVA-ZrP-Cs_1SWA hybrid membrane. Proton conductivity is steadily increasing with temperature for both the hybrid membranes and for comparison the corresponding data for Nafion® 115 measured at 100 % relative humidity is included in Fig. 3.

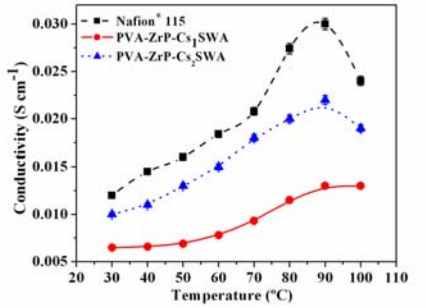

Fig. 3 Proton conductivity at 50 % RH as a function of temperature for hybrid membranes compared with Nafion® 115 at 100 % RH

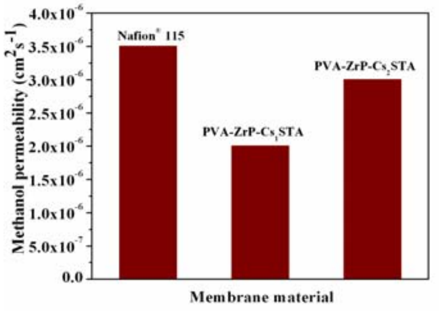

Fig. 4 Methanol permeability of hybrid membranes compared with Nafion® 115

The concentration of crossed methanol as a function of crossover time is determined for PVA–ZrP–Cs_1STA and PVA–ZrP–Cs_2STA hybrid membranes and it is compared to Nafion® 115. In the case of hybrid membranes there is an exponential increase in crossover whereas in the case of Nafion® 115 it is linear with respect to crossover time. Among the two hybrid membranes PVA–ZrP–Cs_2STA shows lesser crossover to methanol. As shown in Fig. 4, the methanol permeability for hybrid membranes was less compared to Nafion® 115. Compared to Nafion® 115, hybrid membranes containing cesium salt of SWA show resistance to methanol permeability with appreciable proton conductivity.

Fig. 5 shows the single cell performance of DMFC with PVA–ZrP–Cs_1STA and PVA–ZrP–Cs_2STA hybrid membranes as proton conducting electrolyte. For comparison, the single cell performance of Nafion® 115 as proton conducting electrolyte under similar condition is also shown. The polarization and power density curves are obtained under unoptimized conditions by a home made passive cell. Electrode area of 2 cm×3 cm with 6 mg cm^{-2} of Pt–Ru black (1:1 atomic ratio, anode) and Pt black (cathode) were fabricated and placed on either side of the membrane. Cell with PVA–ZrP–Cs_2STA hybrid membrane delivers a maximum power density of 6 mW cm^{-2} which is comparable to that of Nafion® 115 (5.4 mW cm^{-2}). The cell with PVA–ZrP–Cs_1STA hybrid membrane exhibited lower performance (2.1 mW cm^{-2}) in full cell mode in comparison to PVA–ZrP–Cs_2STA hybrid membrane and Nafion® 115. The open circuit voltage (OCV) for the cell with PVA–ZrP–Cs_2STA hybrid membrane is 0.652 V and that for PVA–ZrP–Cs_1STA hybrid membrane is 0.619 V. The increase in OCV compared to Nafion® 115 (0.610 V) indicated reduced methanol crossover to the cathode side. The results suggest that these membranes may be suitable for application in DMFC.

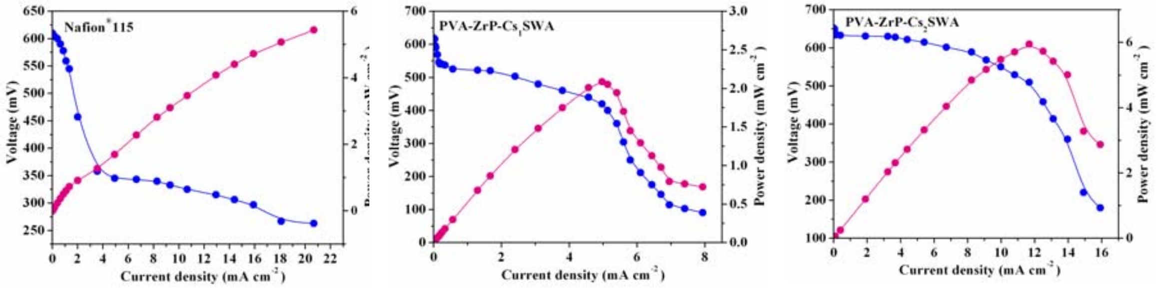

Fig. 5 Polarization and power density curves for passive DMFC cell with Nafion® 115, PVA-ZrP-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes as proton conducting electrolyte at RT and at atmospheric pressure

4.3 Cesium salts of heteropoly acid embedded poly(vinyl alcohol) (PVA)-polyacrylamide (PAM) organic-inorganic hybrids as possible electrolyte for DMFC application.

PVA membranes with appropriate swelling properties along with good proton conductivities are needed for use in fuel cells. Increase in water content in the membranes would result in loss of dimensional stability and cause an increase in methanol permeability. Polymer swelling can be reduced by blending, cross-linking or copolymerizing with other suitable polymers, while proton conductivity can be increased by forming hybrids by incorporating proton conductors like heteropoly acids.

In the present investigation, we report on the formulation and fabrication of a new class of hybrid membranes containing cesium salt of different heteropoly acids such as phosphomolybdic acid (PMA, *MW*: 5,000,000, Otto Kemi, India), phosphotungstic acid (PWA) and silicotungstic acid (SWA) incorporated into the poly(vinyl alcohol) (PVA)-polyacrylamide (PAM) blend. It is for the first time PVA-PAM polymer matrix has been proposed and chosen by us in order to formulate hybrid membrane material with salts of heteropoly acid. A simple fabrication route was adopted in the preparation of these hybrid materials. These membranes are characterized through various physicochemical techniques, morphological studies and permeability experiments. The suitability of these membranes for direct methanol fuel cell application has been explored by carefully investigating various required key characteristics of the membrane such as proton conductivity, water uptake and ion-exchange property.

From water uptake, swelling and ion exchange capacity studies of these materials, it has been found that the extent of water uptake of PMA containing hybrid membrane is higher (66%) compared to other hybrid membranes with PWA (50%) or SWA (48%). The water uptake capacity of these studied hybrid membranes are two to three fold higher compared to Nafion® 115 membranes. At the room temperature (RT), the swelling extents of all the fabricated hybrid membranes were found to be nearly four to six folds lesser compared to the commercial Nafion® 115 membrane, while maintaining higher water uptake due to the presence of hydrophilic property of the heteropoly acid materials. A drastic decrease in the swelling extent of the fabricated PVA based hybrid membrane was attributed appreciably due to the interpenetrating network that has been formed in presence of PAM and glutaraldehyde. Ion exchange capacities (IEC) of the hybrid membranes were slightly lower compared to the commercial Nafion® 115 polymer electrolyte membrane due to their inherent chemical compositions.

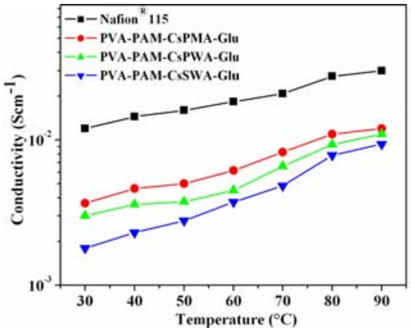

Fig. 6 Proton conductivities of the fabricated hybrid membranes and Nafion®115 at different temperatures

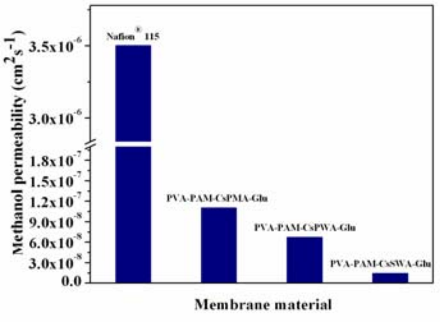

Fig. 7 Methanol permeability of fabricated hybrid membranes compared with Nafion®115

Fig. 6 shows the proton conductivity characteristics of the fabricated hybrid membranes measured at varying temperatures ranging from 30 to 90 °C. Among the hybrid membranes studied, cesium salt of PMA substituted hybrid membranes exhibited higher conductivity compared to cesium salts of PWA and SWA substituted systems. In particular, PVA-PAM-CsPMA membrane exhibited the highest proton conductivity in the range of 10^{-2} S cm^{-1} at 50 % RH. For comparison the proton conductivity of commercial Nafion® 115 polymer electrolyte membrane measured at 100 % RH is shown. The presence of salt of heteropoly acid as well as highly acidic N-H proton of polyacrylamide with hydrogen bonded interpenetrating network of the polymer matrix leads to a facile proton transport through the membrane under low humidity. The order of proton conductivities of the hybrid membranes is in accordance with the water uptake ability and IEC of the materials. Proton conductivity of the fabricated hybrid membranes were lesser compared to the state of the art Nafion® 115 membrane. Perfluorosulphonate proton exchange membranes such as Nafion® membrane materials enjoy the status of premium proton conductivity among all membrane materials due to their inherent chemical composition.

The rate of crossed over methanol appeared to vary with the variation in incorporated heteropoly acid material. Hybrid membrane containing silicotungstic acid, SWA as an active component exhibited lower rate of methanol crossover compared to other heteropoly acid materials such as phosphotungstic acid, PWA or phosphomolybdic acid, PMA containing hybrid membranes. The concentration of crossed methanol through PVA-PAM-CsSWA-Glu hybrid membranes after 180 min was three fold lesser than with that of PVA-PAM-CsPWA-Glu and four times lower than with that of PVA-PAM-CsPMA-Glu system. Fig. 7 shows the quantitative representation of methanol permeability of the hybrid membranes and the results were compared with that of commercial Nafion® 115 membrane. Methanol permeability is an order of magnitude lesser for the fabricated hybrid membranes compared to Nafion® 115. This may be due to the dense interpenetrating network that was formed due to the blending of PVA with PAM followed by crosslinking with glutaraldehyde.

Heteropoly acids possess a unique conceptual character called ‘Pseudoliquid phase behavior’ in which polar molecules like methanol can be readily absorbed into the solid matrix. Hence the fabricated heteropoly acid containing hybrid membranes exhibit the capacity to retain methanol without letting it to pass by. The number of methanol molecules adsorbed per anion is approximated to integral number of protons in the heteropoly molecule (Okuhara *et al.*, 1989). The order of methanol adsorption per Keggin unit was reported to be as follows: $SiW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-}$ which has been clearly reflected in our results on permeability studies.

The membranes exhibited desired properties for DMFC application such as low methanol crossover, optimum swelling with desired proton conductivity with an additional advantage of cost effectiveness compared to present commercial Nafion® membranes.

4.4. Development of hybrid membrane materials with cesium salts of various heteropoly acids in poly(vinyl alcohol) (PVA)- polyacrylonitrile (PAN) matrix for DMFC application

In the present investigation, we report on the formulation and fabrication of a set of new hybrid membranes containing cesium salt of different heteropoly acids such as phosphomolybdic acid (PMA), phosphotungstic acid (PWA) and silicotungstic acid (SWA) into the poly(vinyl alcohol) (PVA)-polyacrylonitrile (PAN) blend. For the first time PVA-PAN polymer matrix has been chosen by us to formulate hybrid membrane material with salts of heteropoly acid. A simple fabrication route was adopted in the preparation of these hybrid materials and the resulting membranes exhibited desired properties for direct methanol fuel cell application such as low methanol crossover, optimum swelling with desired proton conductivity, excellent additive and oxidative stability with an additional advantage of cost effectiveness compared to present commercial Nafion® membranes. These membranes are characterized through various physicochemical techniques, morphological studies and permeability experiments. The suitability of these membranes for direct methanol fuel cell application has been explored by investigating various required key characteristics of the membrane to be employed for fuel cell applications such as proton conductivity, water uptake and ion-exchange property.

Fig. 8 shows the proton conductivity of the fabricated hybrid membranes measured at varying temperatures ranging from 30 to 80 °C. Among the hybrid membranes studied, cesium salt of PMA substituted hybrid membranes exhibited higher conductivity compared to cesium salts of PWA and SWA substituted systems. In particular, PVA(90)-PAN(10)-CsPMA membrane exhibited the highest proton conductivity in the range of 10^{-1} S cm^{-1} at 50 % RH surpassing the state of the art Nafion® 115 measured at 100 % RH. The order of proton conductivities of the hybrid membranes is in accordance with the water uptake ability of the materials.

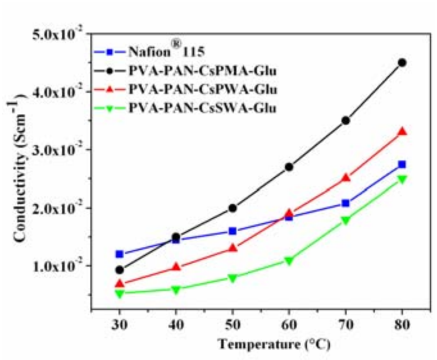

Fig. 8 Proton conductivities of the fabricated hybrid membranes and Nafion®115 at different temperatures

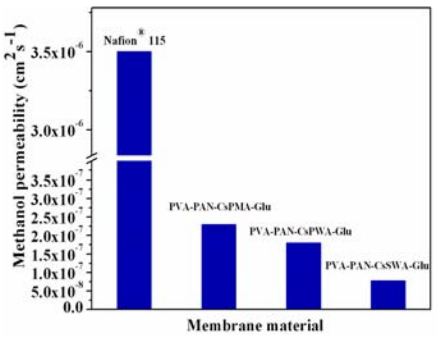

Fig. 9 Methanol permeability of fabricated hybrid membranes compared with Nafion®115

The rate of crossed over methanol appeared to vary with the variation in incorporated heteropoly acid material. Hybrid membrane containing silicotungstic acid, SWA as an active component exhibited lower rate of methanol crossover compared to heteropoly acid materials such as phosphotungstic acid, PWA or phosphomolybdic acid, PMA containing hybrid membranes. Fig. 9 presents the quantitative representation of methanol permeability of the hybrid membranes and the results were compared with that of commercial Nafion® 115 membrane. Methanol permeability is an order of magnitude lesser for the fabricated hybrid membranes compared to Nafion® 115. This may be due to the dense interpenetrating network that was formed due to the blending of PVA with PAN followed by crosslinking with glutaraldehyde.

The increasing order of methanol permeabilities of the membrane materials can be given as: PVA-PAN-CsSWA-Glu < PVA-PAN-CsPWA-Glu < PVA-PAN-CsPMA-Glu << Nafion® 115 (Fig. 9). The fabricated heteropoly acid containing hybrid membranes exhibit the capacity to retain methanol without letting it to pass by due to the 'Pseudoliquid phase behavior' of heteropoly acids. The methanol permeability values of the membrane materials were consistent with those of acid strengths of the corresponding materials that were reflected in IEC measurements. As reported in literature (Okuhara *et al.,* 1989), the acid strength governs the amount of methanol adsorbed on heteropoly acid. The number of methanol molecules adsorbed per anion is approximated to integral number of protons in the heteropoly molecule (Okuhara *et al.,* 1989). The order of methanol adsorption per Keggin unit was reported to be as follows: $SiW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-}$ which has been clearly reflected in our results on permeability studies. Compared to Nafion® 115 membrane, other commercial membranes as well as related hybrid membranes, fabricated hybrid membranes exhibit excellent tolerance to methanol permeability with appreciable proton conductivity.

4.5. Effect of blend density on the properties of poly(vinyl alcohol) (PVA)-polyacrylonitrile (PAN) matrix with cesium salts of heteropoly acids investigated as electrolytes for DMFC application

PVA membrane is poor proton conductor (10^{-6} S cm^{-1}) and extremely swells in water and aqueous methanol. Increase in water content in the membranes would result in loss of dimensional stability and cause an increase in methanol permeability. Polymer swelling can be reduced by blending, cross-linking or copolymerizing with other suitable polymers, while proton conductivity can be increased by forming hybrids by incorporating proton conductors like heteropoly acids.

A series of hybrid membranes has been formulated by blending poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN) followed by cross-linking with glutaraldehyde. Cesium salt of different heteropoly acids such as phosphomolybdic acid (PMA), phosphotungstic acid (PWA) and silicotungstic acid (SWA) were incorporated into the polymer network to form organic-inorganic hybrid membranes. The effects of blend density on water uptake, swelling, proton conductivity and methanol crossover were discussed. The proton conductivity of the hybrid membranes were in the range of 10^{-3} to 10^{-1} S cm^{-1} measured at varying temperatures ranging from 30 to 80 °C and 50 % RH. In particular, PVA(90)-PAN(10)-CsPMA membrane exhibited the highest proton conductivity in the range of 10^{-1} S cm^{-1} at 50 % RH surpassing the state of the art Nafion® 115 measured at 100 % RH. The blend density of the polymer matrix also affects the proton conductivity. Increase in blend density of the polymer matrix decreases the proton conductivity (Fig. 10). With increase in blend density, the proton mobility and the size of the free volume could be restricted resulting in the low proton conductivity.

The interpenetrating network formed by blending of PVA with PAN leads to an order of decrease in methanol crossover compared to state of the art Nafion®115 membrane. With increase in blend density the free volume of the hybrid membranes is restricted leading to low swelling and methanol crossover as shown in Fig. 11. The difference in methanol permeability between the fabricated hybrid membranes containing different cesium salt of heteropoly acids is found to be governed by the adsorption ability of the respective heteropoly acids.

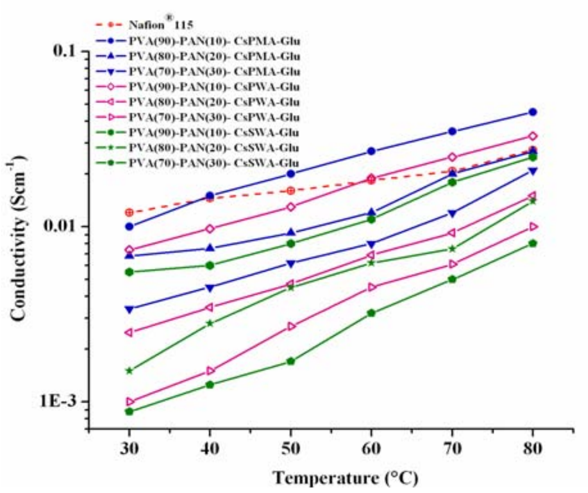

Fig. 10 Temperature dependence conductivity of hybrid membranes with different blend density

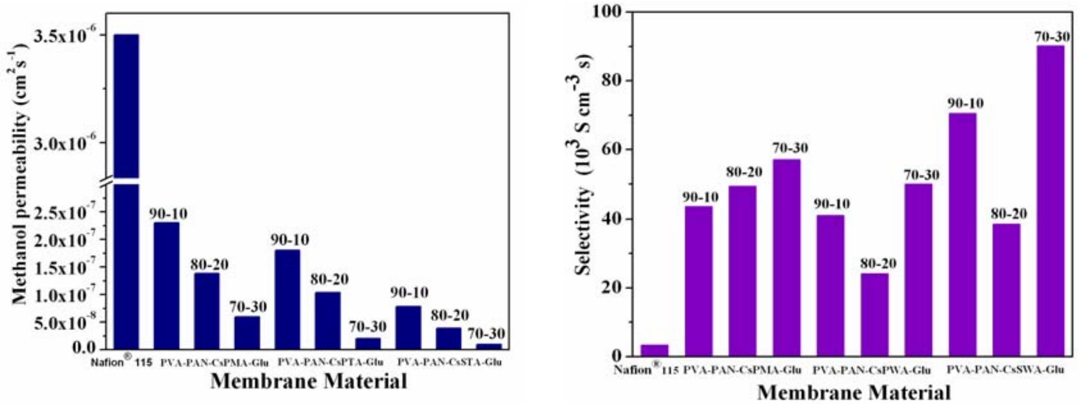

Fig. 11 Methanol permeability and selectivity of hybrid membranes compared with Nafion®115

The high selectivity (proton conductivity/methanol permeability) of the hybrid membranes is attributed to the dense interpenetrating network that is formed leading to low methanol permeability as shown in Fig. 11. These results have proved its potential applicability as polymer electrolyte membrane material for DMFC application.

5. CONCLUSIONS

- The present investigation has shown that hybrid membranes may satisfy the requirements as membrane for DMFC possibly better than the highly conducting commercially available Nafion® membrane.
- Formulation and fabrication of poly(vinyl alcohol) based hybrid membranes with key properties desired for DMFC applications such as low methanol crossover, low swelling, good oxidation stability and with appreciable proton conductivity were demonstrated.

- The enhanced ion exchange capacities and reasonable water uptake characteristics endowed the studied hybrid membrane materials with appreciable proton conductivity.
- Though a number of reports are available in literature on stabilizing the HPA in membrane matrix, a combined approach of hybrid formation with salts of HPA has been explored for the first time.
- The interpenetrating network formed by the blending of PVA with PAM and PAN followed by crosslinking with gluteraldehyde leads to an order of decrease in methanol crossover and swelling compared to state of the art Nafion®115 membrane.
- The difference in methanol permeability between the fabricated hybrid membranes containing different cesium salt of HPA is found to be governed by the adsorption ability of the respective HPA.
- The effect of blend density on various key properties of the membrane towards DMFC application was investigated by fabricating a series of hybrid membranes by blending poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN) followed by cross-linking with glutaraldehyde. Cesium salt of different heteropoly acids were incorporated into the polymer network to form organic-inorganic hybrid membranes.
- With increase in blend density the free volume of the hybrid membranes is restricted leading to low swelling and methanol crossover. The high selectivity of the hybrid membranes is due to the dense interpenetrating network that is formed leading to low methanol permeability.
- These hybrid materials appear as promising candidates for application in DMFC due to their reduced methanol crossover property, which is considered as a major drawback with the expensive fluorine based commercial state of the art Nafion® 115 membranes

- Though the possibility of employing these membranes in practical fuel cells has been demonstrated, their utility in power generation stacks and the viability of commercial exploitation have yet to be ascertained.

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6. PROPOSED CONTENTS OF THE THESIS

Chapter 1	Introduction
Chapter 2	Experimental methodology
Chapter 3	Fabrication and properties of hybrid membranes based on silicotungstic acid, α-zirconium phosphate and poly(vinyl alcohol).
Chapter 4	Fabrication and properties of hybrid membranes based on salts of silicotungstic acid, α-zirconium phosphate and poly(vinyl alcohol).
Chapter 5	Cesium salts of heteropoly acid embedded poly(vinyl alcohol) (PVA)- polyacrylamide (PAM) organic-inorganic hybrids as possible electrolyte for DMFC application.

Chapter 6	Development of hybrid membrane materials with cesium salts of various heteropoly acids in poly(vinyl alcohol) (PVA)-polyacrylonitrile (PAN) matrix for DMFC application.
Chapter 7	Effect of blend density on the properties of poly(vinyl alcohol) (PVA)- polyacrylonitrile (PAN) matrix with cesium salts of heteropoly acids investigated as electrolytes for DMFC application.
Chapter 8	Summary and conclusions

7. LIST OF PUBLICATIONS

1. **Viswanathan, B., M. Helen** and **S. Srinivasa Murthy** (2005) Noble metal based anodes for polymer electrolyte membrane fuel cells. Review Book, Editor. Satoshi Kaneco, Japan, *Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel* 61-104.
2. **Helen, M., B. Viswanathan, L. Himakumar,** and **S. Srinivasa Murthy** (2006) Strategies for the design of membranes for fuel cells. Review Book, Editor. Satoshi Kaneco, Japan, *Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel* 1-42.
3. **Helen, M., B. Viswanathan** and **S. Srinivasa Murthy** (2006) Fabrication and properties of hybrid membranes based on salts of heteropoly acid, Zirconium Phosphate and Poly(vinyl alcohol). *J. Power Source* **163,** 433–439.
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5. **Viswanathan B.** and **M. Helen** (2007) Is nafion, the only choice? *Bull. Catal. Soc. India* **6,** 50-66.

Conference Presentations

1. **Viswanathan B.** and **M. Helen, "**Strategies for the design and fabrication of membranes for fuel cells" Presented in National seminar on challenges in fuel cell Technology: India's perspective, at IIT Delhi, India, on 1st & 2nd December 2006.
2. **Helen**, **M., "**Membrane Catalysis" Presented in Joint Research Fellows Workshop, at IIT Madras, India, on 2nd August 2008.
3. **Helen, M., B. Viswanathan** and **S. Srinivasa Murthy,** "Nanocomposite membranes for DMFC applications" Presented in International conference on functional materials, at Indian Institute of Technology Madras, India, during 27th-29th November 2008, (**Best Poster Award**).
4. **Helen, M., B. Viswanathan** and **S. Srinivasa Murthy,** "Polyoxometalate based membranes for possible DMFC applications" Presented in Hybrid Materials 2009, First International Conference on Multifunctional, Hybrid and Nanomaterials, at Tours, France, during 15th -19th March 2009.