

# Synthesis and Characterization of Solid $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP Membrane for Fuel Cell Applications

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**Abstract:** A novel polymer network membrane composed by  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP was prepared to improve the proton conductivity of PVP membrane. Its physico-chemical properties were characterized using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and solid-state nuclear magnetic resonance (NMR). XRD data shows that the crystallinity increases with increase in concentration of  $\text{SiO}_2$  and  $\text{ZrO}_2$ . Our results indicate the formation and interconnection of ion clusters. It is observed that this new membrane exhibits better proton conductivity as compared to the pristine membrane making them suitable for fuel cell applications.

**Keywords:** Sol-gel, Polyvinylpyrrolidone,  $\text{ZrO}_2$ , Proton conductivity, FTIR, NMR.

## INTRODUCTION

Solid electrolyte is generally employed in fuel cells as an ion-conducting polymer membrane. It has polymer bearing sulfonate or carboxylate groups [1, 2]. Conducting polymers are nowadays considered to be important candidates for the development of polymer devices such as batteries, fuel cell, transducer, biosensor etc [3]. Polyvinylpyrrolidone (PVP) has good film-forming and adhesive behavior on many solid substrates to form a thin film and it also exhibits good optical quality, and mechanical strength required for fuel cell applications. The amorphous structure of PVP also provides a low scattering loss, which makes it as an ideal polymer for composite materials for fuel cell applications. PVP is preferred to avoid phase separation in the reactions because it is easily soluble in water [4-6].

During the last several years, various types of crystalline or amorphous organic or inorganic fast proton conductors were chemically prepared [3]. First group of proton conductors are perovskite-type sintered oxides, which exhibit appreciable proton conductivities above room temperature [4-6]. The second group consists of certain inorganic heteropolyacid hydrates or organic perfluorinated ionomers which exhibit high proton conductivities at low temperatures [7, 8]. Consequently, an improvement in the proton

conductivity of the electrolyte membrane, even by one order of magnitude, could dramatically change the performance of the fuel cells [9]. The proton conductivity of conducting polymer could be improved by suitable fillers. Oxide fillers have excellent properties to enhance the proton conductivity [10]. It would be interesting and also useful to focus research work for the development of fuel cells on low cost materials such as conducting polymers. The objective of our work is to develop an improved novel functional polymer composite membrane for fuel cell applications. In our present work, an inorganic-organic material composite (Nafion/cross-linked PVP semi-interpenetrating polymer network membrane) with improved proton conductivity and a water retention capacity was developed [11]. The synthesized polymers were studied for their structural, morphological, optical and thermal properties.

## EXPERIMENTAL DETAILS

X-ray diffraction patterns of the polymer composite membrane films were recorded for  $2\theta$  values ranging from  $5^\circ$  to  $60^\circ$  with a scanning speed of  $1^\circ \text{ min}^{-1}$  using an X-ray diffractometer (Rigaku Multiflex Japan). The percentage of crystallinity and structure of the polymeric films were investigated using X-ray diffraction measurements. The surface morphology of the nanoparticles in the polymeric films was recorded by a scanning electron microscope (Hitachi S 3500N). The polymeric films were gold-coated under vacuum for SEM measurement.

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The chemical bonds of pure and polymer composites membranes were investigated by Fourier Transform Infrared spectrometer (JASCO, FTIR 460) in the wavelength range from 400–4000  $\text{cm}^{-1}$ . Thermogravimetric (TGA) studies were performed by using DTG 50 from Shimadzu instrument under nitrogen atmosphere. The polymeric samples were heated in the temperature ranging from 300 to 600 K with a constant heating rate of 10 K. This heating results in weight loss, which is recorded as a function of temperature in the TGA thermogram.  $^1\text{H}$  MAS NMR spectra were recorded at 7.05 T (Tesla) using a Fourier-transform NMR (FT-NMR) Varian UNITY INOVA300 spectrometer (Varian, USA).

## RESULTS AND DISCUSSION

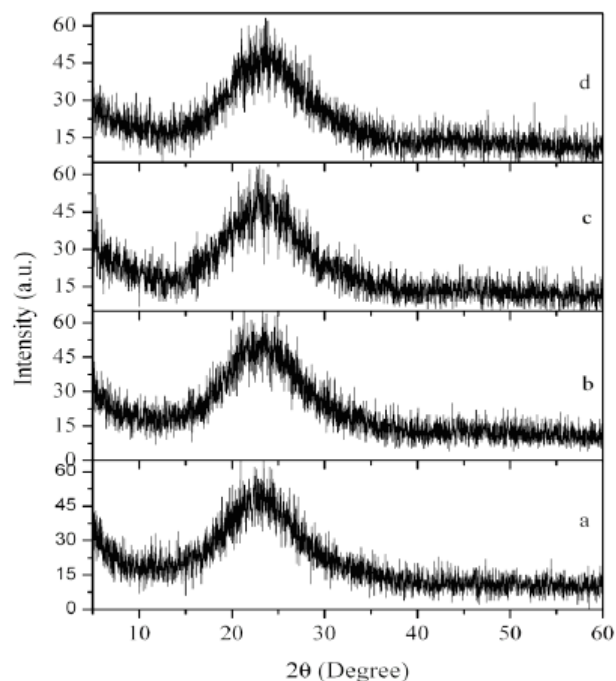
### Structural Studies

Figure 1 shows the X-ray diffraction patterns of various compositions of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP hybrid composite membranes. It is observed from the Figure 1 that the composite films show amorphous nanocrystalline nature in accordance with the reported results in the literature [12–14]. A broad peak centered at  $23.25^\circ$  is observed for films with all the compositions indicating the amorphous nature of the composite films. Neither the appearances of new peaks nor peak shifting are observed in the polymeric composite films; however, intensity of the peaks was found to decrease slightly with increase in  $\text{ZrO}_2$  in PVP. The effect  $\text{ZrO}_2$  on the structural properties with various contents of nanoparticles in PVP membranes was investigated. The percentage of crystallinity ( $B$ ) and average crystallite size ( $L$ ) are calculated from the most intense peak at about  $23.25^\circ$  by using the following relations [12, 13].

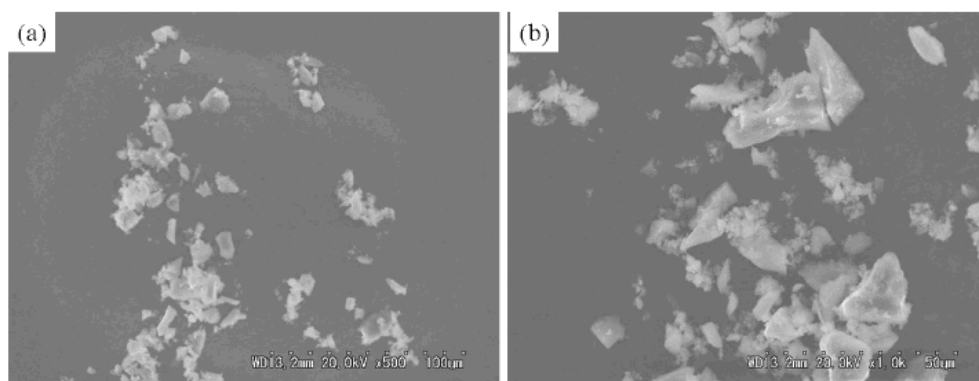
$$B = \frac{A}{A'} \times 100\% \quad (1)$$

$$L = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

The crystallinity is attributed to the restricted effect of the cross-linked PVP polymer chain network on the oxide fillers, and the reduction of free volume in the composite membrane. Thus the polymer chains of PVP are forced to rank orderly and exhibit higher crystallinity with increasing percentage of  $\text{SiO}_2$  and  $\text{ZrO}_2$ .



**Figure 1:** XRD patterns of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP hybrid composite membranes: (a) 94/5/1 mol%–1 g, (b) 93/5/2 mol%–1 g, (c) 92/5/3 mol%–1 g and (d) 91/5/4 mol%–1 g.



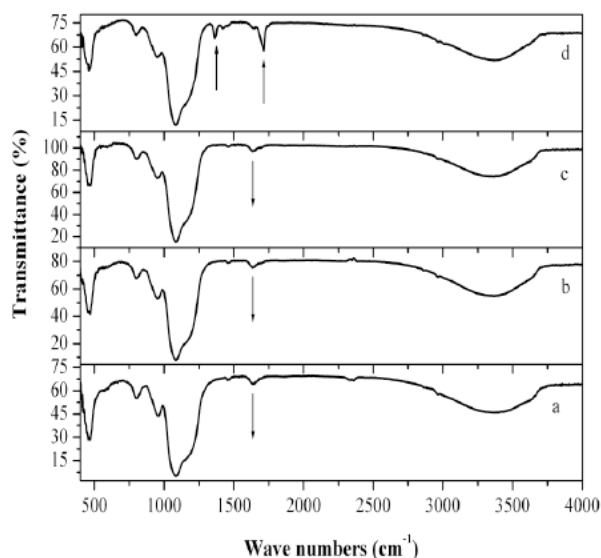
**Figure 2:** SEM images  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP (94/5/1 mol%–1 g) hybrid composite membranes.

## Surface Morphological Studies

The dispersion of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$  nanoparticles in PVP matrix was studied by recording scanning electron micrographs. Figure 2 shows the  $\text{ZrO}_2$  filler is uniformly dispersed in PVP matrix.  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$  nanoparticles and PVP are seen in the form of white and gray regions, respectively in the scanning electron micrographs. The sizes of the  $\text{ZrO}_2$  nanoparticles are found with higher content of  $\text{SiO}_2$  in the  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2\text{-PVP}$  (94/5/1 mol%-1 g) hybrid composite membrane.

## Fourier Transform Infrared (FTIR) Studies

The vibration modes of chemical bonds are characterized by the absorption bands of infrared spectroscopy. The chemical structures of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$  with different contents of nanoparticles in PVP matrix are characterized with the help of Fourier transform infrared (FTIR) spectroscopy as shown in Figure 3. The symbol  $\uparrow$  represents cross-linking and  $\downarrow$  represent chain scissoring. It is clear from the Figure 3 that two new peaks were observed at higher contents of  $\text{ZrO}_2$  at wavenumber 1360.29 /cm ( $\text{ZrO}_2$ ) and 1713.85 /cm (C=O stretching) indicating cross-linking while at 1638.20 /cm (C=O stretching) and chain scissoring.

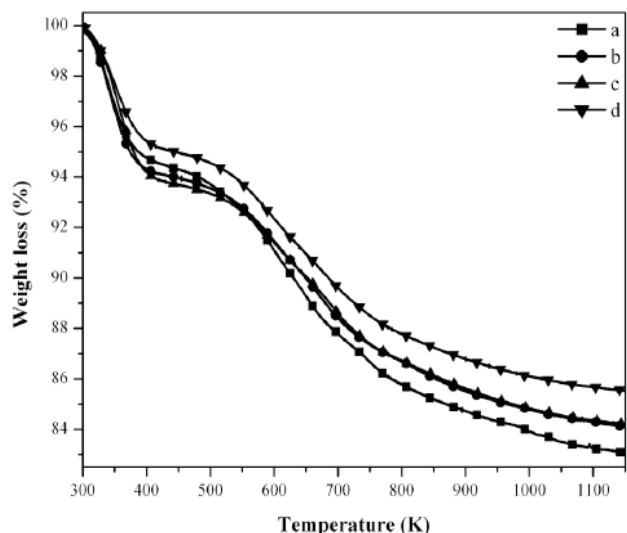


**Figure 3:** FTIR spectra of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2\text{-PVP}$  hybrid composite membranes: (a) 94/5/1 mol%-1 g, (b) 93/5/2 mol%-1 g, (c) 92/5/3 mol%-1 g and (d) 91/5/4 mol%-1 g.

## Thermo Gravimetric Studies

Figure 4 shows TGA curve of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$  fillers in PVP

matrix. Thermogravimetric curves present four regions associated with different weight loss. A first region, between 300 K and 350 K, shows an average loss of 10 % in all cases. Minimum weight loss is observed for  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2\text{-PVP}$  (91/5/4 mol%-1 g), however, maximum loss is observed for  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2\text{-PVP}$  (94/5/1 mol%-1 g). This loss is attributed to desorption of physically absorbed water from PVP and sol-gel oxides, and residual solvents.



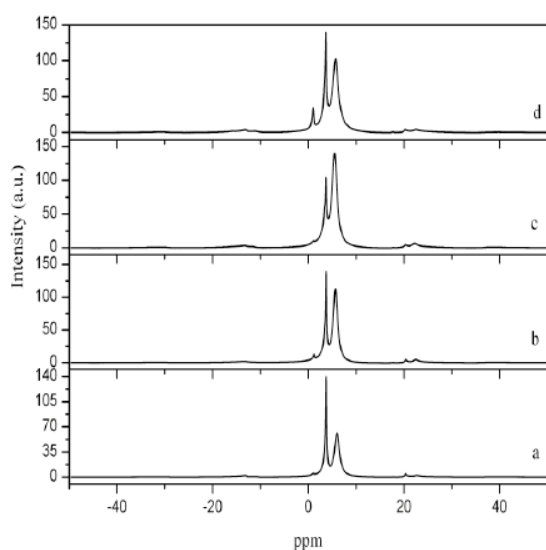
**Figure 4:** TGA thermograms of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2\text{-PVP}$  hybrid composite membranes: (a) 94/5/1 mol%-1 g, (b) 93/5/2 mol%-1 g, (c) 92/5/3 mol%-1 g and (d) 91/5/4 mol%-1 g.

The second region, between 350 K and 500 K, presents a slight weight loss (around 2 %), may be assigned to the release of more structural water from composite matrix and water generated during sol-gel reactions [15, 16]. In the third region, in the range 500–750 K, the TGA curve shows an important weight loss (~ 7%) which may be attributed to an oxidative decomposition of organic residues from unhydrolyzed ligands bound to metals, and combustion of pyrrolidone, and a loss of phosphorous due to the structure collapse of PVP.

In the last region, above 750 K, the weight keeps up very small up to 1050 K and then stable 1150 K. The small weight loss observed at low temperatures indicates that the thermal stability of these inorganic membranes is quite sufficient and will be stable enough within temperature range of fuel cell application. A maximum temperature of 500 K can be used with this membrane for fuel cell application in order to maintain enough water molecules for proton conduction and avoid the degradation of PVP clusters [17, 18].

## NMR Studies

NMR spectra of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP hybrid composite membranes are shown in Figure 5. In NMR spectra, when the percentage of  $\text{ZrO}_2$  is increased while the concentration of  $\text{SiO}_2$  is correspondingly decreased in hybrid membrane of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP, steric effect is produced due to the shifting of protons close to polyaromatic isomer at 7.2 ppm. When a molecule attracts a proton by some force close to other protons and becomes deshielded, it shows dispersion interactions with the variation of semiconducting oxidative compound  $\text{SiO}_2$ . Therefore, it may be concluded that the lone pairs on nitrogen or oxygen in PVP are anti to a C-H band, the proton is shifted in downfield direction due to a decrease in the concentration of  $\text{SiO}_2$  in the hybrid membrane. NMR spectrum shows another peak band at 0.8 ppm due to alkane hydrogens far away from the electron withdrawing group due to aromatic nitro group (*i.e.* - $\text{CH}_3$ ). The peak shows the transfer of protonation in the hybrid membrane structure. Furthermore, the spectra of PVP hybrid membrane strongly reveal that the additions of certain proportions of silica to zirconia have resulted into a densification of the microstructure membrane. As the doping level of  $\text{ZrO}_2$  is increased with decrease in the concentration of  $\text{SiO}_2$ , the protonation in the hybrid membrane is shifted in the direction of downfield and creates the smaller gap between the atoms. The analysis of different functional group is done through NMR and presented in Table 1.



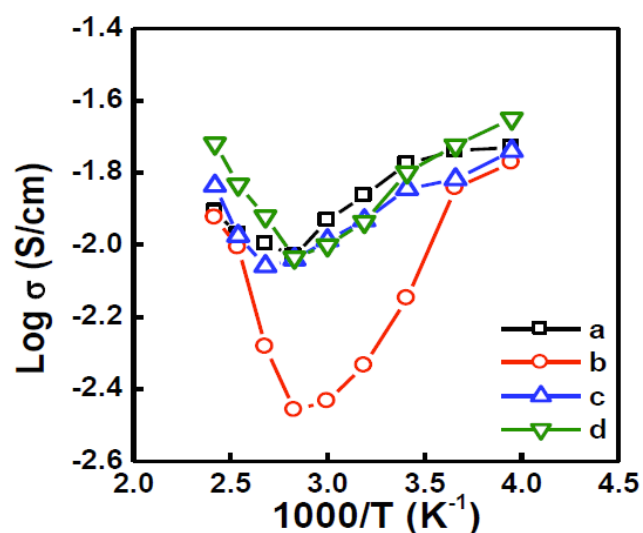
**Figure 5:** NMR spectra of pure PVP and with different contents of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP hybrid composite membranes: (a) 94/5/1 mol%-1 g, (b) 93/5/2 mol%-1 g, (c) 92/5/3 mol%-1 g and (d) 91/5/4 mol%-1 g.

**Table 1:**  $^1\text{H-NMR}$  Characterization of Hybrid Composite Membrane of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP

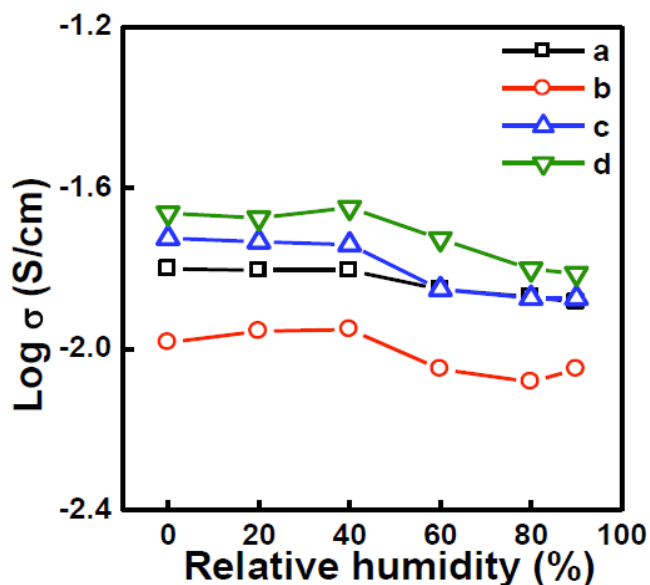
S.No	Functional groups	$^1\text{H-NMR}$ peak
1.	polyaromatic isomer	7.2 ppm
2.	-CH	2.5 ppm
3.	Alkane hydrogen far away from electron withdrawing group (- $\text{CH}_3$ )	0.8 ppm

## Proton Conductivity Studies

Proton conductivity of the composite membranes at different temperatures was calculated from AC impedance spectroscopy studies. Figure 6 shows the proton conductivity of PVP with different filler ratio at different temperatures. The characteristics show two regions such as (i) higher temperature region (*i.e.*, 2.4 K to 2.8  $\text{K}^{-1}$ ) and (ii) lower temperature region (*i.e.*, 2.8 to 4  $\text{K}^{-1}$ ). The proton conductivity decreases in higher temperature region, however, it increases significantly in lower temperature region. Lower temperature region indicates the operating temperature region of fuel cell membrane. The appreciable increase in conductivity is caused by increase of chain length with the temperature. It is noted the conductivity is minimum for  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP (93/5/2 mol%-1 g) system and this might be attributed to the increasing size of cluster boundaries. This situation arises due to a non-homogeneous mixing of all components in composite membranes. The conductivity of composite membrane does not get affected up to 40 % relative humidity as



**Figure 6:** Proton conductivity of  $\text{SiO}_2/\text{P}_2\text{O}_5/\text{ZrO}_2$ -PVP hybrid composite membranes at different temperatures: (a) 94/5/1 mol%-1 g, (b) 93/5/2 mol%-1 g, (c) 92/5/3 mol%-1 g and (d) 91/5/4 mol%-1 g.



**Figure 7:** Proton conductivity of SiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>-PVP hybrid composite membranes at different humidity: (a) 94/5/1 mol%-1 g, (b) 93/5/2 mol%-1 g, (c) 92/5/3 mol%-1 g and (d) 91/5/4 mol%-1 g.

shown in Figure 7; however, it slightly changes beyond 40 % and up to 100 % relative humidity. This indicates that the performance of cell would not be affected by a lower humidity (up to 40 %). SiO<sub>2</sub> and ZrO<sub>2</sub> act as a catalyst for anode and cathode in PVP; however P<sub>2</sub>O<sub>5</sub> acted as a binder of SiO<sub>2</sub> and ZrO<sub>2</sub>. This catalyst prevents the oxygen from accessing the catalyst layer and this causes the increase in proton conductivity with temperature.

## CONCLUSION

Various concentrations of SiO<sub>2</sub> and ZrO<sub>2</sub> were added in PVP with P<sub>2</sub>O<sub>5</sub> to improve its performance as a polymer electrolyte of fuel cell at different operating temperature and humidity. The origin of increasing proton conductivity and analysis of different functional groups are observed by <sup>1</sup>H NMR. The proton conductivity increases due to contribution of protons by various components of composite membrane and also the temperature. The increase in crystallinity with increase in concentration of SiO<sub>2</sub> and ZrO<sub>2</sub> may be contributed to the increase of cluster size. Due to the interaction between sulfonic acid groups and amine groups the composite membranes became more compact. Hence, the inter-cluster crystalline size distance decreased with the increasing content of SiO<sub>2</sub> and ZrO<sub>2</sub> which lead to the cut down of water uptakes and decrease of proton conductivity at higher temperature region. TGA results show that appreciable

thermal stability is achieved due to formation of composite membrane. Therefore, considering the overall performance of the composite membranes, we conclude that the SiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>-PVP hybrid composite membranes are promising candidates for fuel cell applications.

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