Synthesis and characterization of Nafion/SiO$_2$ - MO$_x$ (M= Ti, Zr, W) nanocomposite membranes by sol-gel reaction for fuel cells

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Abstract. Development of efficient and durable cation exchange membranes for fuel cells is important particularly a method for inhibiting the volatility of water at higher temperature is a crucial issue. Nafion composite membranes were prepared by impregnation with SiO$_2$, SiO$_2$ – TiO$_2$, SiO$_2$ – WO$_3$, and SiO$_2$ – ZrO$_2$ by immersing these in-situ sol-gel solution and stirring. The sol-gel solution mixture served to swell the pores of the membrane to maximize the adsorption of the precursor solution. The composite membranes have been characterized by X-ray diffraction, scanning electron microscopy, water uptake, ion exchange capacity and conductivity. XRD studies showed the crystallinity and particle sizes of oxides. FTIR showed the bond formation in oxide mixtures. SEM provides information about the morphology of the particles. Water uptake increased gradually from pure membrane to SiO$_2$, SiO$_2$ – TiO$_2$, SiO$_2$ – WO$_3$, and SiO$_2$ – ZrO$_2$ particles added membranes and was maximum for SiO$_2$ – ZrO$_2$ added membrane. Composite membranes exhibited higher water uptake, ion exchange capacity, conductivity and can improve the efficiency and durability of PEM fuel cells considerably.

1. Introduction
Polymer electrolyte membrane fuel cells are very important energy sources particularly in transportation [1-2]. With the increase in temperature efficiency of fuel cells should increase but proton conductivity of mostly used membranes decreases and it is one of the major obstacles to increase the efficiency of fuel cells. Mostly used cation exchange membranes in fuel cells are Nafion membranes [3] Nafion membranes are expensive, unstable at higher temperatures and are proton conducting when soaked in water and their operational temperature is upto 80 $^\circ$C – 90 $^\circ$C only. It has been reported that gas crossover of nafion also increases with temperature [4]. Considerable efforts are being done to develop membranes for operation at higher temperatures [5]. Higher temperatures have many advantages including faster electrode kinetics and better tolerance to impurities in fuel gas [6-7]. At higher temperature the proton conductivity of Nafion membrane decreases due to dehydration because proton conduction in the membrane depends on the dissociation of protons from SO$_3$H group in the presence of water [8-9]. Development of nanocomposites by inserting inorganic oxides into Nafion which may retain relative humidity in the membranes even at temperatures at or above 100$^\circ$C [10-12]. A lot of work has been done to improve the Nafion membranes for use at higher temperatures [13-15]. Incorporation of metal oxides nanoparticles into Nafion to increase its protonic conductivity and operation at higher temperature have been investigated by adding silica, zirconia and titania etc. [5, 15-16]. It has been shown that addition of silica particles by in situ sol-gel reaction enhanced the
performance of membrane [17]. It has also been reported that addition of zirconia and titania enhanced the performance of the membrane and could be used at 110°C [18-19].

In this study nanoparticles SiO₂, SiO₂-ZrO₂, SiO₂-TiO₂ and SiO₂-WO₃ were impregnated onto the nafion membrane via in situ sol-gel technique. The nanocomposite membranes were characterized for water uptake, ion exchange capacity, FTIR, XRD, SEM, and conductivity.

2. Materials and Methods

2.1. Chemicals
Commercially available nafion resins, nafion membrane, Tetraethylorthosilicate, Tetrabutyl-n-titanate, Zirconium chloride and tungstate were used as received without further treatment.

2.2. Equipment
Fourier transforms infrared (FTIR) spectrometer, Model No, FTSW 300 MX, manufactured by BIO-RAD was used to record Infrared (IR) spectra. Scanning Electron Microscopy was carried out using JSM 5910, JEOL Japan. X-ray diffraction pattern of all samples were obtained at room temperature by using X-ray Diffractometer (3040/60 X’pert PRO) using Ni-filtered cu-Kα radiations (40 kV, 30mA). For elemental analysis, energy dispersive X-ray (EDX) spectrometer EDX-720/800 Hs/900 Hs was used. Conductivity was measured using two probe technique.

2.3. Synthetic procedure for SiO₂-MOₓ (M=Ti, Zr, W) nanocomposite membranes by in-situ sol gel method
Received Nafion membrane was boiled in 3% H₂O₂ solution for 1 hour. That membrane was rinsed with deionized water at 80°C for 30 minutes. Membrane was immersed in 1 M H₂SO₄ solution for 1 hour at 80°C. Membrane was rinsed with deionized water and was dried in vacuum oven for 6 hours. After the treatment Nafion membrane was dipped into precursor solution of Tetraethyl Orthosilicate: Methanol (3:2 vol%). Membrane was washed with methanol and was dried at 80°C. Using similar protocol SiO₂-MOₓ (M=Ti, Zr, W) nanocomposite membranes were synthesized using Tetrabutyl-n-titanate, Zirconium chloride and tungsten solution as precursors followed by same procedure as mentioned for SiO₂-nanocomposite membrane.

2.4. Water uptake measurements
Water uptake values of the Nafion nanocomposite membranes were determined. Different pieces of the nanocomposite membrane were prepared using the following steps: membranes were heated at 105 ⁰C for 1 h and then at 50 ⁰C for 24 h in an oven; then, the membranes were cooled down to room temperature weighed immediately and then soaked in deionized water at room temperature for 24 h. The membrane was removed, gently wiped with tissue paper, and weighed again. The water uptake was calculated by following formula: The water uptake (WU% ) =\( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \). Where \( W_{\text{wet}} \) is the weight of the wet membrane and \( W_{\text{dry}} \) is the weight of the dried membrane [9].
3. Results and Discussions

3.1. Synthesis of anocomposite membranes

Infiltration of Nafion membranes with SiO$_2$ and MO$_2$ has been studied [20]. In this work, Tetraethylorthosilicate solution was added to the methanol solution containing Nafion membrane. SO$_3$·H$^+$ group catalyzes the sol-gel reaction and TEOS molecules migrate to the sulfonic acid group clusters. Then, the membrane is cured at 100 $^\circ$C and condensation of SiOH groups takes place [21].

3.2. FTIR studies of Nafion nanocomposite membrane synthesized by sol gel method

IR spectrum of Nafion membranes showed absorption band at 1195.0 cm$^{-1}$ which corresponds to C-F asymmetric stretching in Nafion membrane. Peak at 1142.9 cm$^{-1}$ corresponds to C-F symmetric stretching and at 538.0 cm$^{-1}$ band corresponds to C-F bending [22]. In Nafion /SiO$_2$ nanocomposite membrane, an absorption band at 792.0 cm$^{-1}$ corresponds to Si-O-Si symmetric stretching. Peak at 1026.6 cm$^{-1}$ corresponds to S-O symmetric stretching as shown in Fig.1. By observation of nafion/SiO$_2$-TiO$_2$ nanocomposite membrane, an additional peak was observed at 969.1 cm$^{-1}$ which corresponds to Si-O-Ti vibration. 1213.6 cm$^{-1}$ corresponds to C-F asymmetric stretching. While peak at 1146.0 cm$^{-1}$ corresponds to C-F symmetric stretching as shown in Fig.2. IR spectrum of Nafion/SiO$_2$-ZrO$_2$ nanocomposite membrane showed an additional peak at 919.3 cm$^{-1}$ corresponding to Si-O-Zr stretching in Nafion composite membrane. Another absorption peak appeared at 1010.6 cm$^{-1}$ corresponding to C-F stretching as shown in Fig.3. IR spectrum of nafion /SiO$_2$-WO$_3$ nanocomposite membrane showed presence of W-O-W vibration group at 726.0 cm$^{-1}$. C-F bending appeared at 558.1 cm$^{-1}$. Peak at 624.5 cm$^{-1}$ showed C-S stretching.

![Figure 1. FTIR spectrum of Nafion/SiO$_2$ nanocomposite membrane](image1)

![Figure 2. FTIR spectrum of Nafion/SiO$_2$-TiO$_2$ nanocomposite membrane](image2)
3.3. XRD analysis
Fig.4 shows the XRD spectra of protonated dry Nafion-115 membrane. It is nearly similar to the XRD reported by [23] for the dry nafion-115 membrane. The broad first peak is indicating the crystalline scattering of the polyfluorocarbon chains in Nafion membranes and their overlapping with the X-ray scattering from the amorphous region of the membrane at lower Bragg angles [24, 25]. XRD spectra for the nanocomposite membrane for Nafion-SiO2-ZrO2 is shown in Fig.5. The peaks are nearly the same but first peak is suppressed and the second peak has been enhanced. Intensity of the original peak is lower in the case of nanocomposite membranes. Nearly similar peaks were obtained for all the other nanocomposite membranes. Nanoparticles have not shown their specific peaks which means that the particles are in small size and also may be in amorphous form.

3.4. SEM and EDX Analysis of nanocomposite membranes
SEM image of pure membrane is shown in Fig.6, and of SiO2-ZrO2 nanocomposite membrane (by sol gel method) in fig.7, and of SiO2-TiO2 in Fig.8 are shown. It can be seen easily that particles had been adsorbed on the surface of Nafion membrane and are just showing physical interaction with membrane. SEM images of SiO2-TiO2 Nafion membrane is indicating the impregnation of binary oxides on surface of Nafion membrane that are also indicating physical interaction and it has been confirmed by FTIR spectrum. The nanoparticles in both the cases can be seen in the micrographs. The particles penetrate into the membrane and have also some interaction with the membrane as confirmed by FTIR but still can be seen in the micrographs. EDX analysis shows that pure Nafion membrane has peaks for carbon fluorine and sulfur only Fig.9, but the EDX for SiO2-ZrO2 shows clearly the
additional peaks of silica and zirconia Fig.10. In Fig.11 is shown the EDX for SiO₂-TiO₂ and it shows the peaks of Titania and silica.

### 3.5. Water uptake

Water uptake of Nafion/SiO₂ - MO₃ (M= Ti, Zr, W) nanocomposite membranes synthesized by sol gel method has been listed in Table 1. By taking under consideration the water uptake values of nanocomposite membranes it was observed that Nafion- SiO₂ membrane showed water uptake 20.7% higher than Nafion membranes. Nafion-SiO₂, WO₃ membrane showed water uptake 53.7% higher...
Table 1. Water uptake by nanocomposite membranes

| Serial number | Commercially prepared membranes | Water uptake (%) |
|---------------|---------------------------------|------------------|
| 1             | Nafion                          | 43%              |
| 2             | Nafion-SiO₂                     | 63.7%            |
| 3             | Nafion-SiO₂-WO₃                 | 96.7%            |
| 4             | Nafion-SiO₂-TiO₂                | 109.24%          |
| 5             | Nafion-SiO₂-ZrO₂                | 121.52%          |

than Nafion membrane. Nafion- SiO₂. TiO₂ membrane showed water uptake 66.24% higher than Nafion membrane. Nafion- SiO₂. ZrO₂ membrane showed water uptake 78.52 % higher than Nafion membrane. The increase in water uptake can be due to the hydrophilic nature of the acidic inorganic additives within the pores of Nafion membrane. The increase in acidity and surface areas of nanoparticles may also be responsible for enhancement of water uptake.

With increase in water uptake from silica to tungsten to titania to zirconia nanocomposite there was an increase in acidic strength. On the basis of results obtained, it can be concluded that incorporation of nanosized acidic inorganic with higher surface areas in Nafion membrane, enhances its water uptake properties. That is a key design objective for high temperature membranes. The incorporation of inorganic additives in PEMs is more beneficial at higher temperatures and lower RHs. Higher water uptake and enhanced acidity also increase proton conductivity, which would result into better fuel cell performance under both hot and dry conditions [26].

3.6. Ion exchange capacity

Ion exchange capacity of Nafion/SiO₂ - MOₓ (M= Ti, Zr, W) nanocomposite membranes synthesized by sol gel method and by solution casting method has been measured. It was observed that Nafion-SiO₂-ZrO₂ sol–gel was the most acidic membrane. This membrane exhibited highest water uptake followed by Nafion-SiO₂, TiO₂, Nafion-SiO₂-WO₃ and Nafion-SiO₂. Ion exchange measurements are in agreement with the water uptake results [15].

3.7. Conductivity measurements

Resistance of Nafion nanocomposite membranes was measured using resistivity meter has been shown in Fig.12. It was observed that resistance of nanocomposite membranes was decreased at high temperature. It was also observed that Nafion-SiO₂-ZrO₂ nanocomposite membrane has low resistance.
as compared to other nanocomposite membranes. Nafion-SiO2-ZrO2 membrane has better water uptake, better ion exchange capacity and now better conductivity. Thus addition of SiO2-ZrO2 improves the properties of the nafion membrane considerably.

![Figure12](image_url)

**Figure12.** Conductivity of composite membranes at different temperatures.

### 4. Conclusions

Impregnation of nafion membrane with nanoparticles by in situ sol-gel method improved the properties of the membrane considerably. Membranes were impregnated with SiO2, SiO2 – TiO2, SiO2 – WO3, and SiO2 – ZrO2 particles by sol-gel method. Water uptake by the nanocomposite membranes increased considerably and it was maximum for SiO2 – ZrO2 impregnated membrane. Thus the membranes will not be dehydrated even at higher temperature and performance of membranes and consequently the efficiency of fuel cells will increase considerably. Ion exchange capacities were also measured and these also showed similar trend. XRD spectra was typical of the dry protonated membrane and absence of peaks for the nanoparticles shows that particles are of small size and of amorphous nature. FTIR spectra of the membranes were taken which showed bond formation between the nanoparticles and membrane which indicates that nanoparticles will not be easily leached out of the membrane. SEM and EDX showed the presence of nanoparticles impregnated onto the membranes. Conductivity of the nanocomposite membranes increased with temperature which shows that the membranes will perform better at higher operational temperatures of the fuel cells. Thus the nanocomposite membranes will improve the efficiency of fuel cells.

### 5. References

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