



A Comparison of Physical, Chemical, Thermal and Electrical Properties of Nafion -117 and Y- Zeolite/Nafion -117 Composite Membranes

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ABSTRACT: The Nafion-117/ Y zeolite membrane were synthesized for proton exchange membrane fuel cell. The physico-chemical, thermal and electrical properties of Nafion and composite Nafion-117/ Y zeolite membrane are compared. The Nafion and composite Nafion-117/ Y zeolite membrane are characterized by XRD, TEM, FT-IR, DSC and proton conductivity. The composite membrane showed increase in proton conductivity relative to Nafion -117 at elevated temperature.

Keywords: Composite membrane, Zeolite, XRD, FTIR, DSC, proton conductivity

I. INTRODUCTION

The proton exchange membrane fuel cells have attracted tremendous attention in recent years because of their highest efficiency compared to other types of fuel cells. Nafion, a perfluorinated polymer substituted by sulfonic acid groups, is the most commonly used polymer for the fabrication in proton exchange fuel cell membranes. Polymer electrolyte fuel cells based upon perfluorinated membranes have typically been operated in a temperature range between approximately 50°C and 90°C [7, 9]. Increasing the operating temperature above room temperature will improve the electrode kinetics of the oxygen reduction reaction [17]. The upper limit of temperature results from the difficulty in maintaining membrane water content at temperatures at or above 100°C. In addition, temperatures above the polymer glass transition temperature (~110°C for protonated Nafion) can cause polymer chain rearrangements, which can lead to structural changes in the membrane and lower the membrane stability, performance, and lifetime [11, 20, 21]). There has been a efforts to develop polymer membranes able to operate above 100°C prompted by the additional benefits of enhanced carbon monoxide (CO) tolerance and improved heat removal [19].

The most significant barrier to running a polymer electrolyte fuel cell at elevated temperatures is maintaining the proton conductivity of the membrane. The increased temperature raises the evaporation rate of water from the membrane and the vapor pressure required to keep a given amount of water in the membrane.

A number of investigators have tried to prevent the loss of water at elevated temperature from the ionic pores of Nafion by modifying the membrane for use in polymer electrolyte fuel cells [1-3],[10],[14],[15] &[18]. One of the method is the doping of hydrophilic metal oxide particle such as SiO₂, ZrO₂, TiO₂ to have water retention property and enhance the conductivity at elevated temperature [4],[12],[13][17]&[19].

Zeolites are micro porous crystalline solids with well defined structure. They contain silicon [SiO₄]⁴⁻, aluminum [AlO₄]⁵⁻, oxygen and water in their framework tetrahedral linked from the corner [8]. Due to the difference in charges between silicon [SiO₄]⁴⁻, aluminum [AlO₄]⁵⁻ in the tetrahedral link will create a negative charge inside the chain. Therefore this negative charge will be neutralized by attracting ion. The zeolite is used as ion exchange and can hydrate with high amount of water [5].

In this research work nanoparticles of Y zeolite were synthesized and then these nanoparticles were incorporated into Nafion -117 forming a composite membrane. The composite membrane was expected to have high water retention and enhance the proton conductivity at elevated temperature. The different structural, physico- chemical and electrical properties of composite membrane were investigated and compared with pure Nafion -117.

II. EXPERIMENTAL

A. Material and membrane preparation

Tetra methyl ammonium hydroxide ($(\text{CH}_3)_4\text{NOH}$) (1M), Aluminium isopropoxide ($\text{C}_9\text{H}_{21}\text{O}_3\text{Al}$) (1M), Tetra methyl ammonium bromide ($\text{C}_8\text{H}_{20}\text{NBr}$), Colloidal silica (SiO_2), Nafion -117 (solution and membrane), 3% Hydrogen peroxide (H_2O_2), 1M Sulphuric acid (H_2SO_4), 1M Phosphoric acid (H_3PO_4), DDI H_2O , Ethyl alcohol.

Preparation of Y- Zeolite: The nanoparticles of Y zeolite were synthesized using the procedure described by Brett A et al [6]. The colloidal suspension of zeolite Y nanocrystals was prepared by taking a 250 mL polypropylene bottle containing a magnetic stirrer. The bottle was washed with double deionized water (DDI H_2O) under ultrasonication. Then 100 ml of DDI H_2O , aqueous tetra methyl ammonium hydroxide (9.115ml) solution and appropriate amount of sodium hydroxide were added, in that order, and stirred vigorously for one hour at room temperature until the solution became clear. Then aluminum isopropoxide (20.43g) was added and stirrer the solution at room temperature and solution was clear in 24 hrs. Tetra methyl ammonium bromide (21.016g) was then added to the clear solution and stirred until completely dissolved. Colloidal silica (6.008g) was then added to complete the solution and bottle was tightly sealed, it was aged for 4 days at room temperature (RT) with vigorous stirring and was heated at 100°C for 8 days in oil bath.

All samples were washed by three repetitions of centrifugation with relative centrifugal force of 15,000 g for 2 h; then decanting, and redispersion in DDI H_2O

with ultrasonication before analyses preparations were performed.

Synthesis of Y Zeolite/ Nafion 117 composite membrane: The composite membranes were prepared using Nafion- 117 as the base material. To obtain a uniform high purity film, membranes were cleaned with a standard treatment procedure: (i) boiling in 3% hydrogen peroxide for 1 hr to oxidize organic impurities; (ii) rinsing with boiling water for several hours; (iii) boiling in 1 M sulfuric acid for 1 hr to remove any metallic/ionic impurities; and (iv) rinsing again in boiling water to remove any excess acid.

The zeolite was incorporated into Nafion using the procedure first described by Grot and Rajendran [10]. Then 20% of Y zeolite(1.35g) solution is prepared in 1M aqueous solution ethyl alcohol (30ml) with constant stirring at room temperature. The membrane was dipped in zeolite solution for 2 days at 60°C . The membranes was then rinsed in cold water to remove the excess zeolite solution from the surface and then immersed in 1 M phosphoric acid (H_3PO_4) overnight at 80°C . The phosphoric acid has the two purposes to re-protonate the sulfonate anions to regenerate the acidity of the membrane. The membranes were then repeatedly boiled for 2 hours in distilled water to remove any excess acid solution.

Synthesis of Y Zeolite - Nafion 117 Powder: The 20% of Y zeolite (1.35g) powder is added 10 ml solution of Nafion -117 and the solution was heated to remove the solvent. Then the precipitated was boiled in 6M sulphuric acid and dry at 80°C for 3hrs. Then the precipitate was calcinate in air at 90°C overnight and crushes the resulting particles.

B. Structural characterization

X- ray diffraction pattern were collected with powder diffractometer using Cu K radiation with 2θ range $5^\circ - 80^\circ$. The FT-IR spectra for the sample were recorded in the range $600-4000\text{cm}^{-1}$ at room temperature. The transmission electron microscopy (TEM) images were collected at room temperature.

C. Proton conductivity

Proton conductivity was measured by four probe method using the relationship $\sigma = d/RtI$, where d is distance between the probes, t and l is the thickness and width of the film, R was derived by ohm,s law $R=V/I$. V and I were found from the apparatus. To determine the conductivity the different samples of the membrane were sandwiched between the electrode and probes in a cell. Then the cell is placed in temperature control chamber under temperature range of 30°C to 150°C .

The current (I) and voltage (V) values were collected at different temperature.

III. RESULT AND DISCUSSION

A. X-ray diffraction

Fig.1 shows the x- ray patterns of Y – Zeolite. The x- ray diffraction peaks at different values of 2θ show the presence of both Y- zeolite and Al_2O_3 phases. Also the high intensity of XRD lines indicates a high degree of crystallinity and homogeneity of the zeolite.

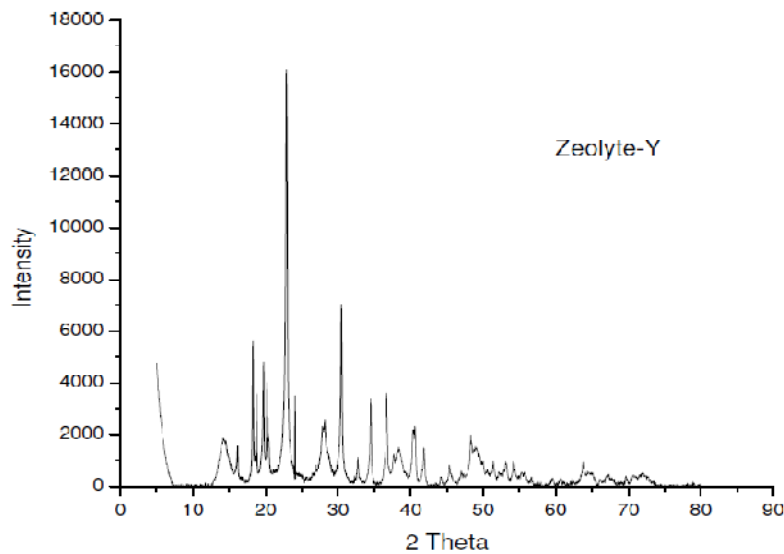


Fig. 1. X-ray diffraction patterns for Y – Zeolite.

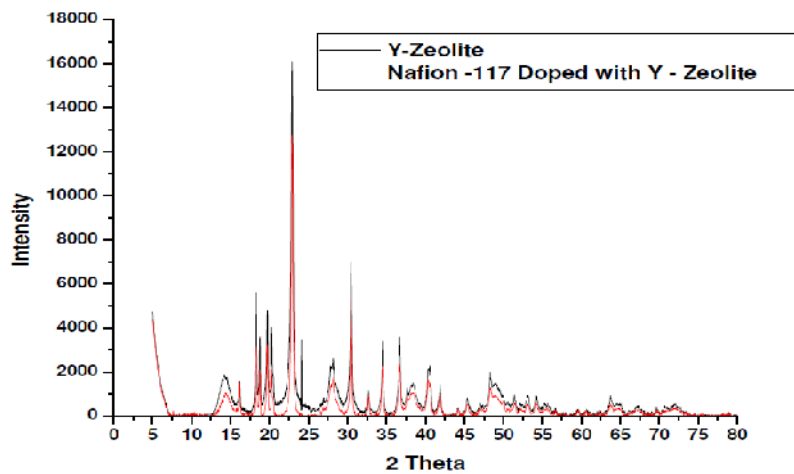


Fig. 2. Comparison of X-ray diffraction patterns for Y – Zeolite and doped Nafion -117/ Y- zeolite.

Fig. 2 shows the comparison of X – ray diffraction pattern of Y – Zeolite and doped Nafion -117 with Y – zeolite. It is observed from the figure 2 we have the similar diffraction peaks but the intensity of each peaks get decreases on doping Nafion -117 with Y- zeolite. This indicates the increase in the amorphous nature of Zeolite material. Broad peaks also indicate the conformation of homogeneity and compatibility among the doped Nafion -117 /Y- zeolite material.

B. Transmission electron microscopy (TEM)

Morphology and size information of Y- zeolite is obtained from the TEM images which are depicted in figure 3a, 3b and 3c. From the figure 3a, 3b, 3c it is observed that cage like structure of y- zeolite. Based on the results obtained from TEM measurement, it was found that particle diameter of 20nm in y- zeolite.

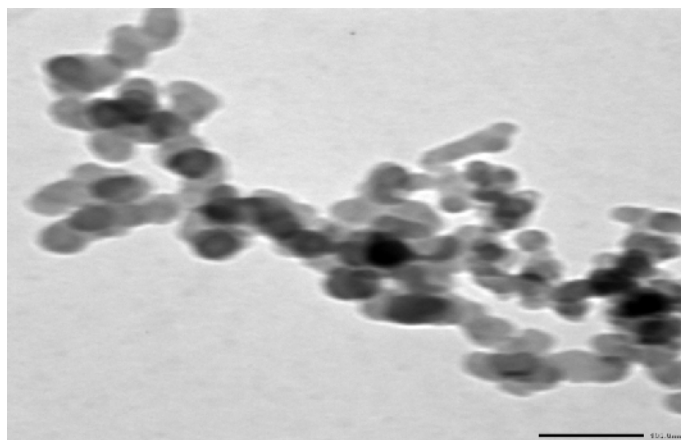
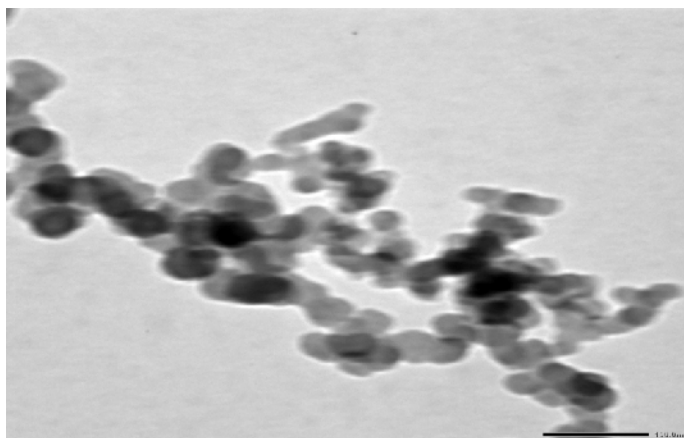
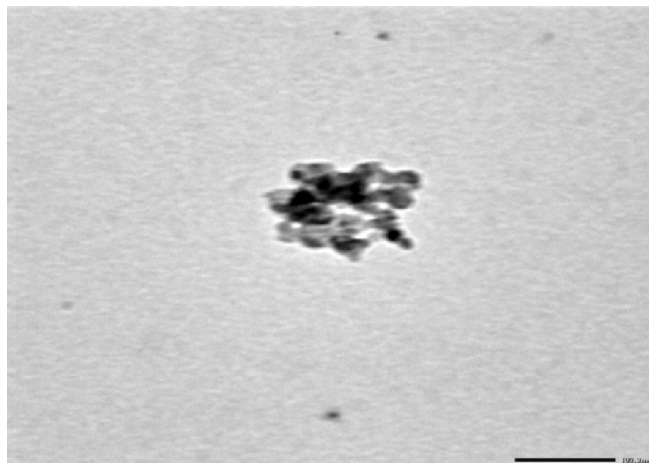


Fig. (3a). TEM Images Y –zeolite.



(b)



(c)

C. FT-IR Spectroscopy

The FTIR spectrum of Nafion117 / Y- zeolite nano composite membrane material is shown in figure 4. The infrared band and their assignment for bare Nafion 117 is given in table 1 [22]. It is observed from the figure 4 the presence of the bands associated with hydronium ion (H_3O^+) are at around 1539cm^{-1} , 1649cm^{-1} and 1735cm^{-1} . This concludes the hydrophobic nature of the composite material. The reason of the presence of these bands is due to the presence of H_2O molecule in the zeolite. The first noticeable difference between Nafion 117 and composite material of Nafion 117 / zeolite is

the presence of bands at bands 3448cm^{-1} , 3277cm^{-1} and 2978cm^{-1} . The band around 3448cm^{-1} , 3277cm^{-1} represent O-H stretching and band around 2978cm^{-1} is for $-\text{COOH}$ stretching, all these band are the characteristics of zeolite. The second difference between Nafion 117 and the nanocomposite is the presence of the band at 734cm^{-1} , 1020cm^{-1} and 1539cm^{-1} . These bands are due to Na_2O , Al_2O_3 and SiO_2 stretching. The positions of vibration modes of all types of M-O bonds are strongly influenced the interaction with polymer and Na_2O , Al_2O_3 and SiO_2 .

Table 1: FTIR Characteristics of Bands of Nafion 117 [22]

Frequency (cm^{-1})	Assignment
1500 -2050	Hydrated H_3O^+
1199	CF_2 asymmetric stretching
1144	CF_2 symmetric stretching
1057	SO_3^- symmetric stretching
981&966	C-O-C stretching
804	C-S stretching

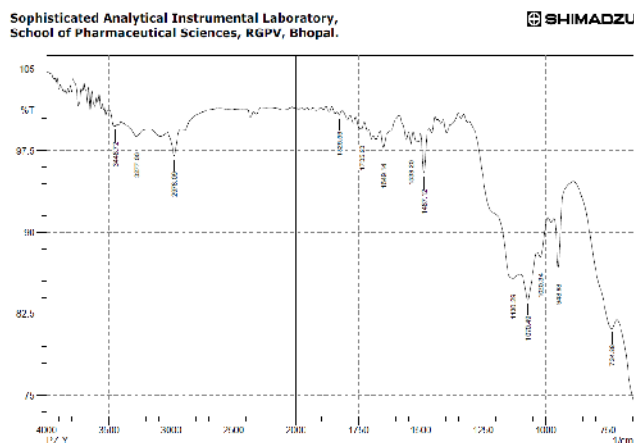


Fig. 4. FTIR spectra of Nafion 117/ Y-Zeolite composite membrane material.

D. Differential Scanning Calorimetry (DSC)

Figure 5 represents a typical DSC diagram of Nafion 117/ Y-Zeolite composite material. From the figure 5 it is observed that the peak maxima for melting and vaporization of freezable water are at around 23^oC and 105^oC respectively. In the region above 105^oC we get

one endothermic peak interpreted as a melting of crystalline backbone at 274^oC. The increases in melting point of in the composite material of Nafion 117/ Y-Zeolite with respect to bare Nafion -117 (200^oC)[22] is due to the cross linked structure of nafion-117 with zeolite molecules.

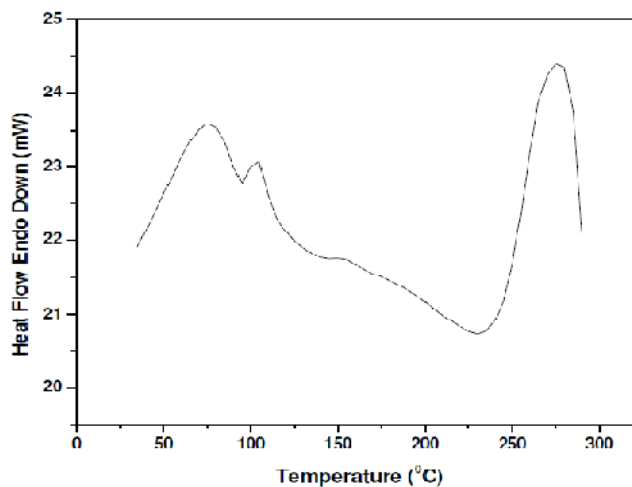


Fig.5. DSC Thermogram of Nafion 117/ Y-Zeolite composite Material.

E. Proton conductivity

The temperature dependence proton conductivity comparison of Nafion -117 and Nafion -117/ Y – Zeolite membrane is shown in the figure 6. It is observed from the figure upto 60⁰C the bare Nafion shows more conductivity than the composite membrane. It is also observed from the figure 6, above 60⁰C the proton conductivity of composite membrane get increased than bare Nafion -117. The improvement

in proton conductivity may come due to hydrophobic nature of composite membrane. The hydrated water increases the motion of proton and hydronium ion which enhances the proton conductivity.

When the temperature is increased from room temperature the proton conductivity increases as shown in figure 6. The maximum value of proton conductivity for composite membrane is obtained 2.1Scm⁻¹ at 95⁰C which is 1.3 Scm⁻¹ times higher than bare Nafion -117.

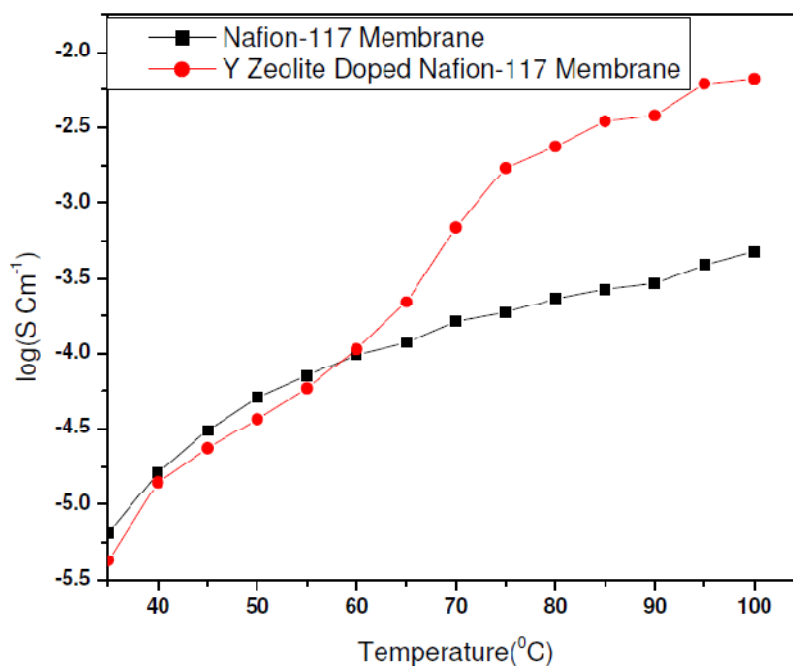


Fig. 6. Temperature-dependent proton conductivity of Nafion -117 and Nafion 117/ Y-Zeolite composite membrane.

IV. CONCLUSION

The nano particles of Y- Zeolite are added in Nafion-117 to Nafion-117/ Y- Zeolite composite membrane. The prepared Nafion-117/ Y- Zeolite composite membrane having better thermal and electrical properties than the bare Nafion-117.

The proton conductivity of composite membrane has been improved 1.3 times than the bare Nafion -117. Also the crystalline melting point of the composite membrane is increased than bare Nafion -117 from 200⁰C to 274⁰C.

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