



Effect of relative humidity on mechanical strength of zirconia/ Nafion[®] Nano-composite membrane

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Abstract

This paper presents the results of mechanical strength of wet and dry zirconia/ Nafion[®] nano-composite membrane. The tensile tests were conducted to determine elastic modulus and stiffness of dry and wet pristine Nafion[®] membrane and modified Nafion[®] membrane. The composite membranes were prepared by recast method of different synthesized zirconium oxide with the zirconia content of 10% by weight. The uniaxial mechanical properties of nano-composite membranes and recast Nafion[®] membrane were captured using a CellScale UStretch uniaxial testing system. The length, width, and thickness of samples were measured using a Vernier caliper and recorded prior to testing. It was found that elastic modulus of the wet Nafion recast is 62.06 %, 35.26 %, 30.79 % and 35.26 % higher than that of Nafion[®]/ Zr-100, Nafion[®]/ Zr-80, Nafion[®]/Zr-50, and Nafion[®]/Zr-0, respectively. The elastic modulus of dry Nafion recast, Nafion[®]/Zr-100, Nafion[®]/Zr-80, Nafion[®]/Zr-50, and Nafion[®]/Zr-0 membranes are 46.29 %, 83.31 %, 64.81 %, 59.84 %, and 78.36 % higher than those of wet Nafion[®] recast, Nafion[®]/Zr-100, Nafion[®]/Zr-80, Nafion[®]/Zr-50, and Nafion[®]/Zr-0 membranes, respectively. Furthermore, the results showed that when the water content increases in the nano-composite membranes the mechanical strength also decreases.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are used in a variety of applications such as stationary, automotive and mobile [1] due to their high efficiency of electrical conversion. PEMFCs use hydrogen or methanol as their fuel to produce electricity without environmental pollution indicating there are no gas emissions,

and only water as the waste product can be reused [2]. The PEMFCs heart is a proton conducting membrane, since this proton conducting membrane conduct protons from the anode electrode to the cathode electrode, without allowing the oxygen and hydrogen gas crossover. Moreover, the fuel cell longevity depends on the mechanical strength of proton conducting membrane, as it must endure any

operational changes such a water content and temperature without any operation failure [3, 4]. Nafion® membrane when operates at lower temperature maintain a high ionic conductivity and mechanical, thermal and chemical stability [5, 6]. It consists of hydrophobic polytetrafluoroethylene (PTFE) backbone and hydrophilic perfluorinated pendant side chains ending with sulfonic groups SO_3H^+ (acid form) [7]. When in contact with water the sulfonic swell and form hydrophilic domain. Critical characteristics of a good polymer electrolyte membrane (PEM) are fast friction conduction, good water transport, thermo-mechanical stability and sustained durability under various operating conditions [7].

Furthermore, the Nafion® membrane because of its chemical structure-function well in its hydrated state, with the proton conductivity decreasing with the increase of temperature and lower relative humidity [8]. But this Nafion® membrane dehydrates at the temperature above 80°C and starts to shrink which leads to the development of cracks, and with a high methanol permeability.

Incorporating various nanoparticles can improve membrane conductivity, water management, mechanical properties, and bring changes to pore and channel structure [9-13]. Zirconium oxide (ZrO_2) has been used in the fuel cell, thermal barrier coating and refractory materials due to its high thermal, chemical and mechanical stability [14]. Nafion® membrane was modified with inorganic fillers such as ZrO_2 to introduce the hydrophilic side of the membrane and enhance the mechanical strength with higher ionic conductivity in order to function on the methanol or hydrogen fuel cell at higher temperature [15-17]. Functioning at higher temperature improves the carbon monoxide (CO) tolerance and reaction kinetics with reduction of catalyst loading on the membrane electrode assembly of fuel cell [18-20]. This eliminates the properties of fuel cell gas, the findings prompt the research on fuel cell working on high temperature. In this paper, mechanical properties of the modified nano-composite membrane are investigated using tensile modulus measurement when the dry and wet state is compared with that of recast

Nafion® membrane, as the wet-up and dry-out can cause significant stresses in the membrane.

2. Experimental

2. 1. Materials

Sodium hydroxide, silver nitrate, N, N-dimethylformamide (Merck), sulfuric acid (Merck), zirconium oxychloride hydrate (Merck), isopropanol (Merck), and Nafion® solution (Sigma) were used as received.

2. 2. Synthesis of ZrO_2 nanoparticles

The ZrO_2 nanoparticles were prepared using precipitation method. Zirconium oxychloride hydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were used as starting materials. 0.2M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was prepared in a 250 ml beaker, and 2N NaOH solution was added drop wise with continuous stirring for 45 minutes.

The obtained precipitate was divided into six parts; one part was filtered and washed several times with distilled water until chlorine ion (Cl^-) was not detected by silver nitrate (AgNO_3). The precipitate was dried at 100°C for 24 hours, followed by calcination at 600°C for 4 hours, and labeled as Zr-0.

Whereas the remaining parts of the solution were covered with a foil and put in an oven at 50°C , 80°C , and 100°C temperatures for 24 hours, after which they were filtered, then washed and calcinated according to the Zr-0 procedure and then stored for analysis. Afterward, the samples were labeled as follows Zr-50, Zr-80, and Zr-100.

2. 3. Preparation of nano-composite membranes

The nano-composite membranes were prepared using 5 % Nafion® solution as the standard material for reference. Nafion® solution (10 ml) with N, N-dimethylformamide (DMF) (20 ml) was mixed to replace solvents. 10wt % of Zr, Zr-50, Zr-80, and Zr-100 nanoparticles were added to the Nafion®/ DMF solution and stirred at room temperature for 2 hours, then were ultrasonicated for 30 minutes [21]. The resulting solution was poured onto a piece of flat glass, and soaked into

an oven at 80 °C for 12 hours to remove the solvent, and finally heated up to 160 °C for 30 minutes. The membranes were then peeled off from the glass plate. Before conducting any measurement, all membranes were kept in deionized water for 12 hours. The thickness of the membranes was measured with a digital micrometer (0.18 cm). Each thickness was measured in the average of 3-7 reading at the different position of a membrane and was repeated twice on each membrane in order to obtain the average value.

2. 4. Water uptake (%) of nano-composite membranes

The membrane were soaked in distilled water for one day. Then was removed, wiped and weighed on a microbalance. Water uptake was calculated according to Eq. (1):

$$W_{up}(\%) = \frac{(m_{wet} - m_{dry})}{m_{dry}} \times 100 \quad (1)$$

where W_{up} is the percentage of water uptake, m_{wet} is the weight of a swollen membrane immediately, and m_{dry} is the weight of the membrane after being dried.

2. 5. Tensile test

The uniaxial mechanical properties of nano-composite membranes and recast membrane were captured using a uniaxial testing system. The length, width, and thickness of samples were measured using a Vernier caliper and recorded prior to testing. The testing area of the membrane samples was 4 mm × 10 mm in dimension. To allow clamping area, the samples were prepared in such a way that they will be clamped on both sides and still allow the testing area to be 4 mm × 10 mm.

A thickness of 0.18 cm of the nano-composite membrane was used in analyzing the stress applied to the sample. The membranes were soaked in water for 24 hours and tested for the wet test. Then the membranes were dried in a vacuum oven at 80 °C for 24 hours and tested for the dry test. The tensile strength of modified Nafion membranes was measured using a

CellScale Ustretch device dried at 25 °C and wet at 34 °C and actuator speed of 5 mm per min.

2. 6. Characterization

X-ray diffraction (XRD) analysis was performed using a Philips X-ray diffraction with CuK radiation source. The analyzed material was finely ground, homogenized, and average bulk composition was determined. Samples were scanned in a continuous mode from 10 - 90° with a scanning rate of 0.026 degree/sec. Thermal properties of the samples and their characteristics were studied by thermal gravimetric analysis (TGA) under nitrogen flow. TGA data were obtained with model STA (Simultaneous Thermal Analyzer) 1500 (supplied by Rheometric Scientific Ltd, UK), over nitrogen and at a heating rate of 10 °C/min from 28 °C to 1000 °C. SEM images were obtained on a Hitachi x650. Electronic techniques were based on the interaction of the sample with electrons, resulted in a secondary effect that was detected and measured.

3. Results and discussion

3. 1. XRD analysis

The modified membranes were characterized by XRD to observe the effect of the zirconia nanoparticles on their crystallinity. The XRD results of modified Nafion® and pristine membrane are shown in Fig. 1. Figure 1(a) shows that the pristine recast membrane has only two reflections peaks at 17.5° and 39° 2theta which resemble the crystallinity within the per-fluorocarbon chains of the ionomer [22].

Figure 1(b) shows the peaks corresponding to the cubic and monoclinic phases of zirconia oxide nanoparticles, also the Nafion® peaks which associated with crystallinity within the per-fluorocarbon chains.

However, Fig. 1(c-e) reflects only the broad diffraction peaks of zirconia cubic phase in the nanosized range without any Nafion® peaks detected. The diffraction peaks at 2theta are 30.2°, 35.2°, 50.6°, 60.2°, 74.2° and 82.5° which correspond to the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 0), respectively [23,

24]. It is noted that the modified membranes obtained more crystallites having bigger size compared to those of the pristine Nafion® membrane. This may be attributed to the crystallites of zirconia nanoparticles that were distributed within the membranes. Furthermore, it is observable in Fig. 1(c-e) that only the crystalline peak of zirconia nanoparticles appears while Nafion® peak disappears.

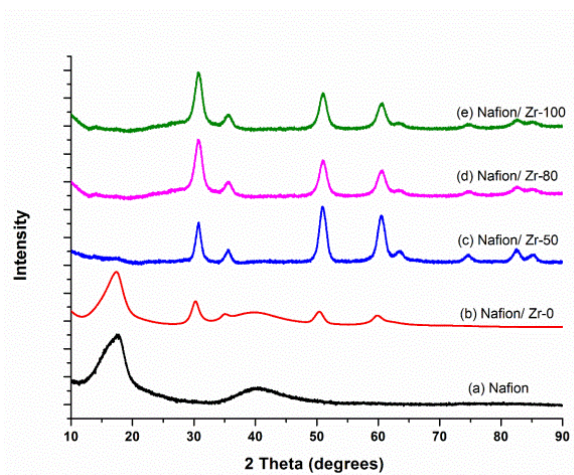


Fig. 1. XRD patterns of the (a) Nafion/ Zr-0, (b) Nafion/ Zr-50, (c) Nafion/ Zr-80, (d) Nafion®/ Zr 100 nano-composite membranes, and (e) Nafion® membrane.

3. 2. Thermo-gravimetric analysis and derivative thermo-gravimetric

TGA and the derivative thermo-gravimetric (DTG) of the nano-composite membrane and pristine Nafion® membrane were conducted to observe weight loss and thermal stability, as displayed in Fig. 2. In Fig. 2(b-e), the modified nano-composite membrane shows three weight loss up to 900 °C due to decomposition of the membrane, with a total loss of 75-94 wt %.

Figure 2(b-e) shows an initial weight loss of about 2% of the original weight below 530 °C, due to the evaporation of hydrated water, and the second weight loss is attributable to the decomposition of the sulfonic acid groups of Nafion® membrane around 550 °C [25]. The third degradation step over 550 °C was assigned to degrade the polymer main chain [21, 26, 27].

Furthermore, the modified Nafion® membrane with zirconia nanoparticles as a filler has a shift in decomposition temperature, Nafion® / Zr, Nafion® / Zr-50, Nafion® / Zr-80, and Nafion® / Zr-100 nano-composite membranes retain its weight up to 510 °C, which shows thermal degradation improvement compared to pristine Nafion® membranes.

The modified Nafion® nano-composite membrane was found to maintain water up to 530 °C, respectively, corresponding to desorption of water from membranes. This result, shown in Fig. 2(b-e), confirms that the modification of Nafion® membrane made by zirconia nanoparticles can improve water retention ability and accelerate the decomposition process of the membrane.

Addition of zirconium oxide improved thermal stability [28] as zirconia nanoparticles were well distributed between Nafion® matrix, as confirmed by XRD and SEM. Because water is a proton-transporting medium for PEMs, the water retention ability above 100 °C is one of the important parameters for fuel cell applications. The pristine Nafion® membranes (Fig. 2(a)) were found to be less stable compared to the modified membrane, (Fig. 2(b-e)) as they started to decompose at a lower temperature of 360 °C.

It is observable in Fig. 2(a) that the pristine Nafion® membranes have three weight loss. The first one is from 50 °C to 360 °C due to the evaporation of hydrated water; the second weight loss is attributable to the decomposition of the sulfonic acid groups of Nafion® membrane [25], and the third one, degradation step over 550 °C, assigns to degradation and combustion of the polymer main chain [21, 26, 27]. The DTG curves of the modified Nafion® and Nafion® membrane illustrate the same two transition peaks which associate with the second and third decomposition stage of a membrane.

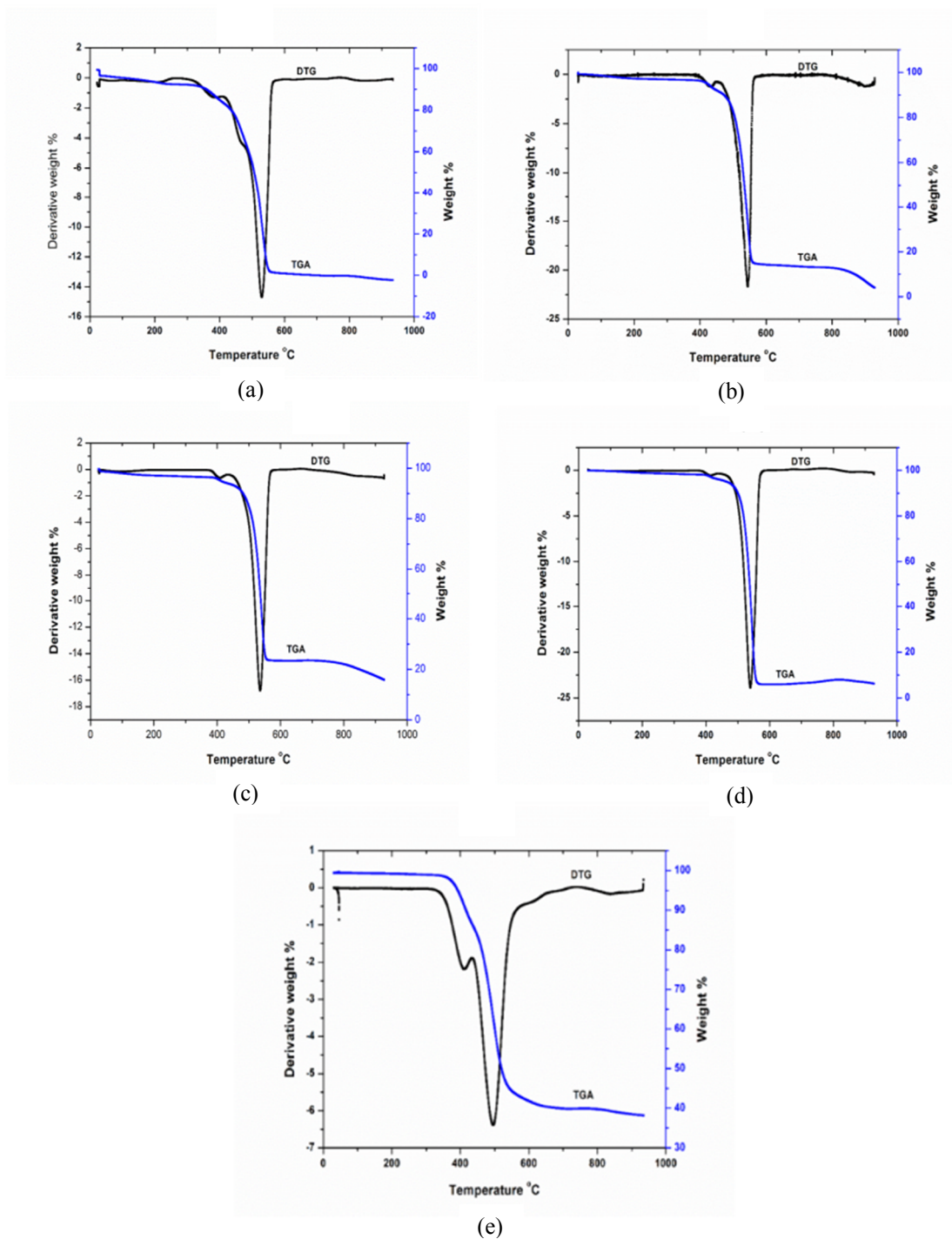


Fig. 2. TGA/ DTG curves of the (a) Nafion[®] membrane, (b) Nafion[®]/ Zr-0, (c) Nafion[®]/ Zr-50, (d) Nafion[®]/ Zr-80, and (e) Nafion[®]/ Zr 100 nano-composite membranes.

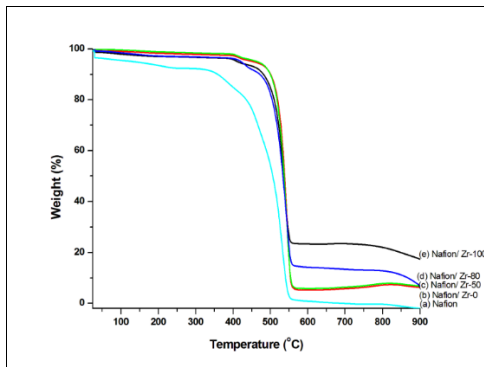


Fig. 3. TGA curves of the (a) Nafion® membrane, (b) Nafion®/ Zr-0, (c) Nafion®/ Zr-50, (d) Nafion®/ Zr-80 and (e) Nafion®/ Zr 100 nano-composite membranes.

3. 3. Tensile test

Force and displacement data were collected at a rate of 5 Hz. The cross-sectional area of the samples was calculated based on membranes thickness and the initial distance between membranes after preloading but prior to testing. Axial force measurements and cross-sectional areas were used to determine stress experienced by the samples in each direction (See Fig. 4). Sample strains in each direction were determined using axial displacements measured by the UniStrecher. A stress-strain relationship was plotted for each sample (See Fig. 4(a, c, e, g, and i)). A force-displacement relationship was also plotted for each sample of the membrane. The stiffness of each membrane was determined by identifying a linear region where its slope is calculated as shown in Fig. 3. The linear regions of the plots were identified and the slopes were calculated to generate a corresponding elastic modulus or stiffness (See Fig. 4 (a-j)). All resultant data was examined and a common linear region, between 0% and 15%, was found. Linear regressions between 0% and 15% were taken for each plot where an R² value of at least 0.9 was required to confirm linearity. Typical stress-strain plots with an applied linear regression in each are shown in Fig. 4 (a-j). The data collected were used to calculate the stress and strain for each of five tests using the force and displacement. The stress-strain of the

modified nano-composite membranes and recast membrane in their wet and dry states are presented in Fig. 4(b, d, f, h, and j). To verify the strain values, the motions of the nano-composites membranes and Nafion® membrane were analyzed using the image analysis toolkit. The image analysis indicated lower strains than the actuator displacement-based strain data. This is not surprising since some of the actuator displacements could have resulted in system deflection and or specimen slippage. When looking at wet membranes, all samples failed at approximately 0.6 strains. When looking at the dry nano-composite membranes, Zr-100 and Zr-0 did not fail at 0.6 strain. The highest stress was recorded on the Nafion® / Zr-100 with an approximately 720 kPa (See Fig. 3(h)), with the more improvement of the yield strength and the elastic modulus, thus demonstrating the close bonding between the zirconia nanoparticles and Nafion® membrane through self-assembly [29]. This improvement of the membrane rigidity demonstrates that the zirconia nanoparticles stabilize the structure of the modified membrane, and give a potential restriction to the humidity-generated stress when the membrane was used as an electrolyte membrane in the fuel cells application Nafion®/ Zr-80 membrane (see Fig. 4 (a-b)) in its dry state shows improvement in stiffness (secant modulus) when compared to recast membrane; this may be due to Zr-80 nanoparticles incorporated in the Nafion which retains water to enhance the mechanical strength of Nafion® membranes. The method for determining the elastic modulus and stiffness of wet and dry nano-composite membranes and Nafion® membrane are shown in Fig. 5. The region selected for determining stiffness is between 0.0 mm and 0.15 mm strain and similarly the region selected for determining stiffness is between 0mm and 1.3 mm. When comparing the elastic modulus of wet Nafion® recast membrane with wet Nafion®/Zirconia, it was found that Nafion® recast is 62.06, 35.26, 30.79, and 35.26% higher than Nafion®/Zr-100, Nafion®/Zr-80, Nafion®/Zr-50 and Nafion®/Zr-0, respectively (See Fig. 5a).

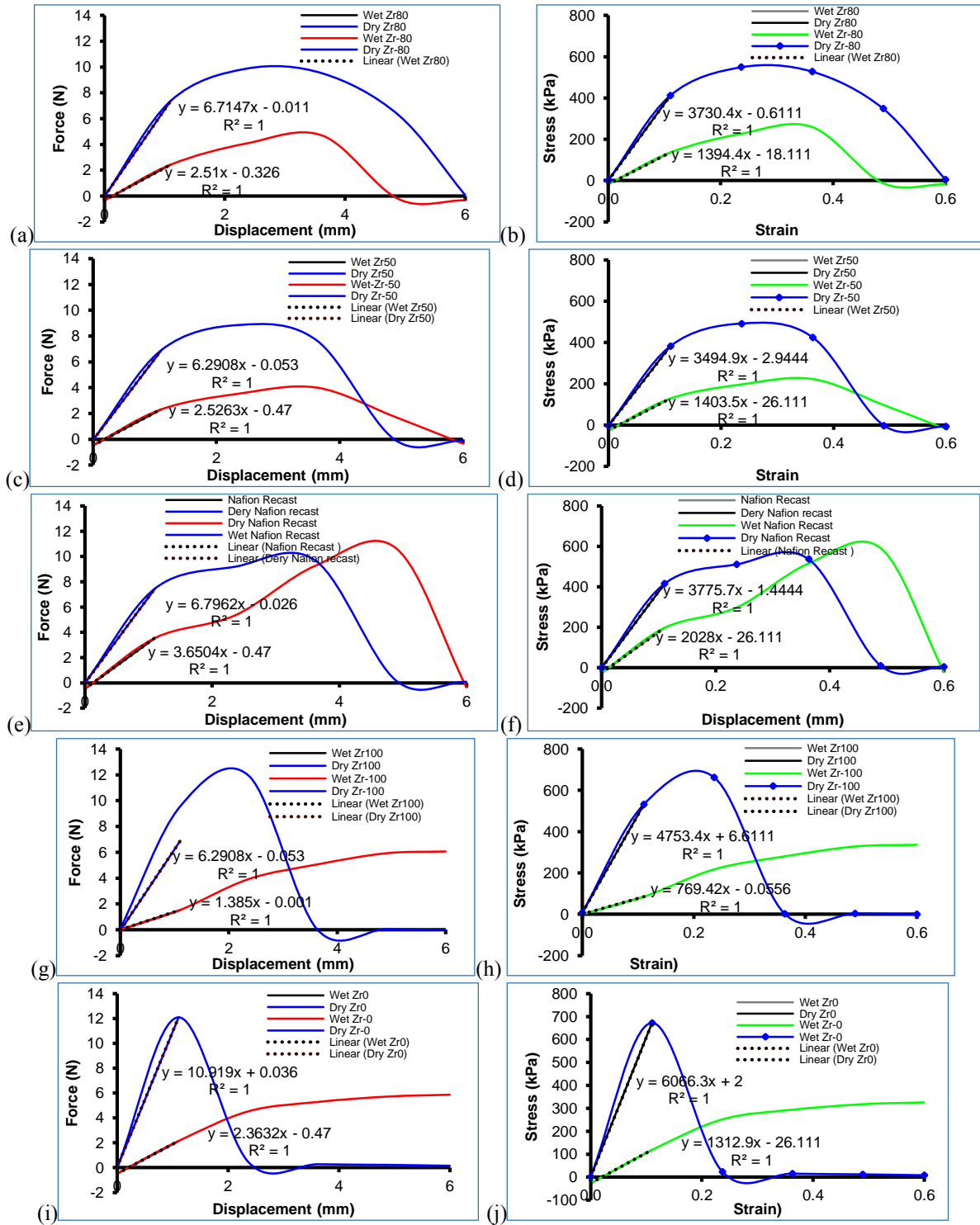
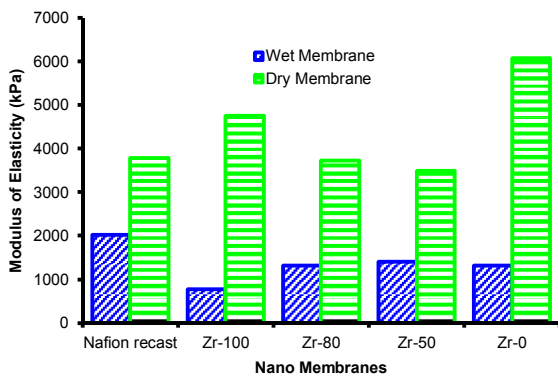
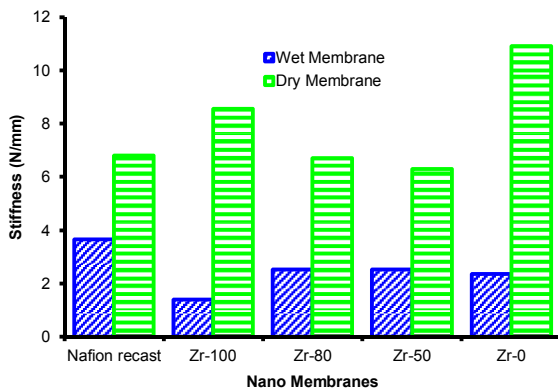


Fig. 4. Mechanical loading response (force-displacement curves) of wet and dry (a) Nafion[®]/Zr-80, (c) Nafion[®]/Zr-50, (e) Nafion[®] recast, (g) Nafion[®]/Zr-100, and (i) Nafion[®]/Zr-0 nano membranes and stress-strain curves of wet and dry (b) Nafion[®]/Zr-80, (d) Nafion[®]/Zr-50, (f) Nafion[®] recast, (h) Nafion[®]/Zr-100, and (j) Nafion[®]/Zr-0 nano membranes. Stress-strain and force-displacement curves show the region where the membrane stiffness was determined (force-displacement region is between 0- 1.2 mm and stress-strain region is between 0-15% strains).

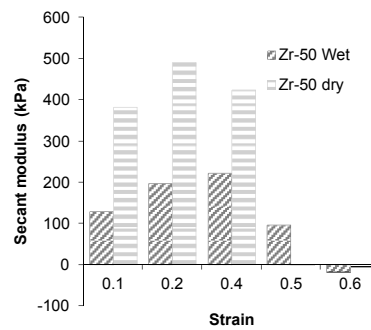


(a)

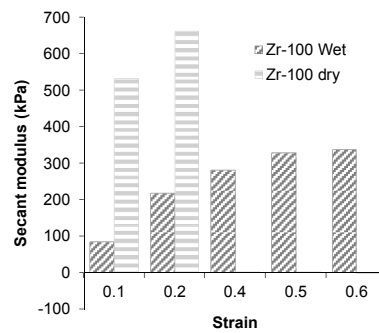


(b)

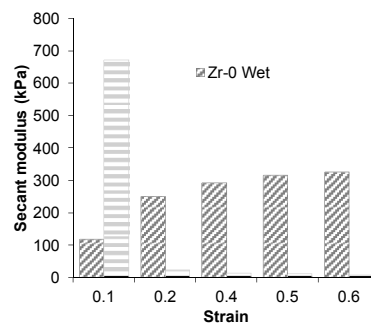
Fig. 5. Modulus of elasticity of dry and wet Nafion[®] and zirconia nano-composite membrane determined at selected region (see Fig. 4 (a) and (b)), the stiffness of dry and wet Nafion[®] and zirconia nano-composite membranes determined at selected region (see Fig. 4).



(c)

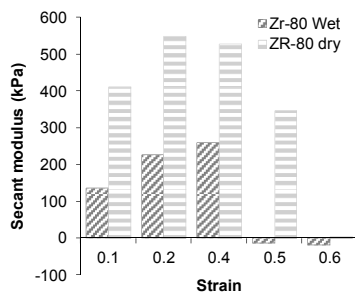


(d)

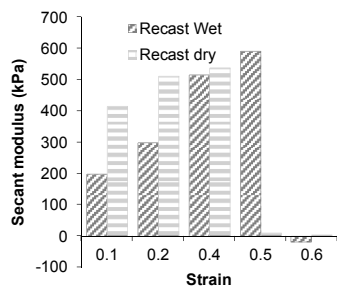


(e)

Fig. 6. Secant modulus of dry and wet (a) Nafion[®]/Zr-80, (b) recast-Nafion[®], (c) Nafion[®]/Zr-50, (d) Nafion[®]/Zr-100, and (e) Nafion[®]/Zr-0, membranes



(a)



(b)

The elastic modulus of dry Nafion[®] recast membrane was found to be 1.20 and 7.44 % higher than Zr-80 and Zr-50, respectively. The elastic modulus of dry Nafion[®] recast membrane was found to be -25.89 and -60.67% lower than Zr-100 and Zr-0, respectively. The elastic modulus of dry Nafion[®] recast, Nafion[®]/Zr-100, Nafion[®]/Zr-80, Nafion[®]/Zr-50, and Nafion[®]/Zr-0 membranes are 46.29, 83.31, 64.81, 59.84, and 78.36 % higher than wet recast Nafion[®], Nafion[®]/Zr-100, Nafion[®]/Zr-80, Nafion[®]/Zr-50 and Nafion[®]/Zr-0 membranes, respectively (See Fig. 6).

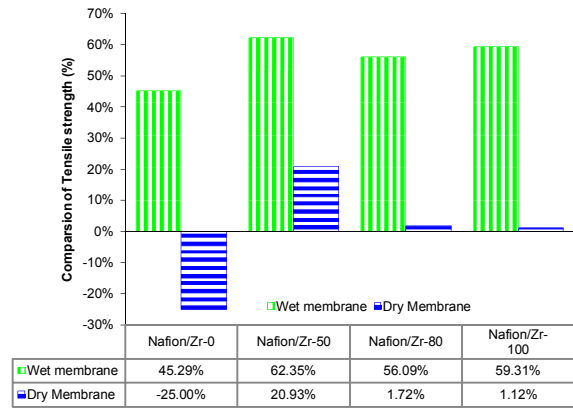
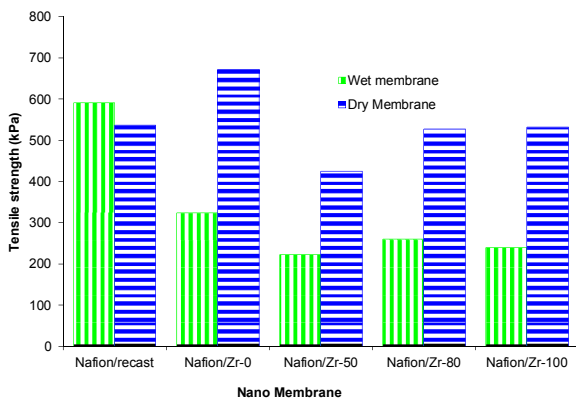
The percentage difference of the elastic modulus of wet and dry membranes is similar to the percentage difference in the stiffness. Generally, the elastic modulus of the dry membranes is higher than that of the wet membranes. Similarly, the stiffness of the dry membranes is higher than that of the wet membranes. The highest stress was recorded in the original Nafion[®] when compared with the nano-composites membranes (see Fig. 3). It was observed that the dry nano-composite membrane has a higher elasticity modulus compared to that of the wet nano-composite membrane. Opposite behavior was observed when compared with the Nafion[®]/Zr-0, Nafion[®]/Zr-50, Nafion[®]/Zr-80 and Nafion[®]/Zr-100 since, in this category, the elasticity modulus of the dry nano-membrane is lower than that of the wet nano-composite membrane (see Fig. 4). The tensile strength of the wet recast Nafion[®] and Nafion[®]/Zr-0 membranes is higher than that of the dry membranes (see Fig. 3). The modulus of elasticity of wet membrane of recast Nafion[®] is 53.8, 45.%, 39.6, and 56.8% higher than the Nafion[®]/Zr-0, Nafion[®]/Zr-50, Nafion[®]/Zr-80 and Nafion[®]/Zr-100, respectively. The modulus of elasticity of dry membrane of recast Nafion is 72.5, 20.6, and 1.8% higher than the Nafion[®]/Zr-0, Nafion[®]/Zr-50 and Nafion[®]/Zr-80, respectively. Ironically, the modulus of elasticity of dry membrane of Nafion is 1.2% lower than that of the Nafion/Zr-100 (see Fig. 7). When comparing the wet membrane of recast Nafion[®], it was observed that recast Nafion[®] is 45.3, 62.4, 56.1, and 59.3% higher than the Nafion[®]/Zr-0, Nafion[®]/Zr-50, Nafion[®]/Zr-80 and Nafion/Zr-100, respectively.

The tensile strength of the dry membrane of recast Nafion[®] membrane is -25.0, 20.9, 1.7, and 1.2% higher than that of the Nafion[®]/Zr-0, Nafion[®]/Zr-50, Nafion[®]/Zr-80, and Nafion[®]/Zr-100, respectively (see Fig. 7). It was found that

the recast Nafion[®] membrane in the wet state has a higher modulus of elasticity and tensile strength when compared to Nafion[®]/Zr-0, Nafion[®]/Zr-50, Nafion[®]/Zr-80, and Nafion[®]/Zr-100 due to its hydrophobic nature. In other words, the tensile strength and modulus increase with increasing water content in the membranes. Moreover, the obtained results show that modified Nafion[®] nano-composite membranes can maintain the mechanical strength when operating in a higher temperature fuel cell, as their elongation at break is higher in the dry state than the wet state. The incorporation of ZrO₂ nanoparticles within Nafion[®] membrane resulted in an increase in tensile strength and modulus. This may be due to the free movement of the membrane chains that was slightly restricted by the intermolecular forces between the membrane chains and the inorganic oxide nanoparticles; the tensile strength of membranes is sequentially enhanced [29].

3. 4. Scanning electron microscopy (SEM)

The scanning electron microscope images of the modified and recast membranes in cross-sections are displayed in Fig. 8. Figure 8(a) presents the micrographs of Nafion[®] /Zr-0 nano-composite membrane with 10wt.% zirconia nanoparticles impregnated within the ionomer of Nafion[®] membrane. It is observable that the nanoparticles are homogeneously distributed within the membrane. Figure 8(b) presents the cross-section image of the Nafion[®] /Zr-50 nano-composite membrane with well distributed and consistent small particles of the Zr-50 nanoparticle. Results in Fig. 8(c-d) show that zirconia nanoparticles consist of sub-micrometric particles with the similar morphology which is well dispersed within the ionomer matrix [30].



(a)

(b)

Fig. 7. (a) Tensile strength of modified Nafion® membranes and (b) comparison of modulus of elasticity.

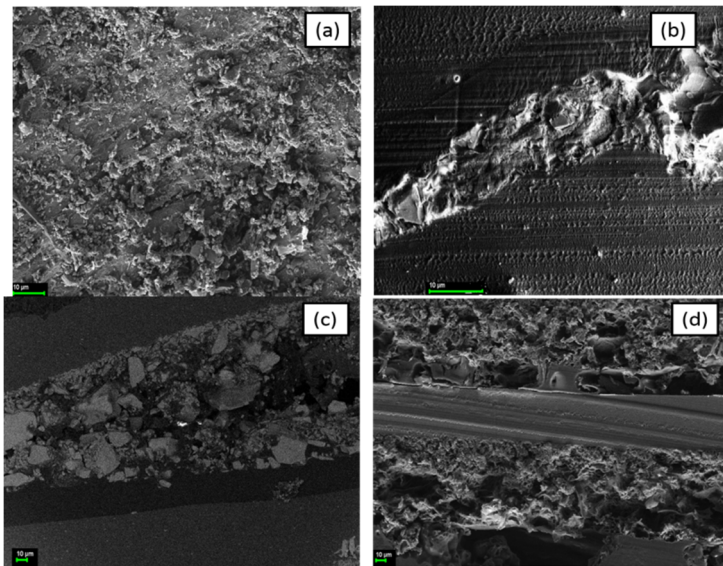
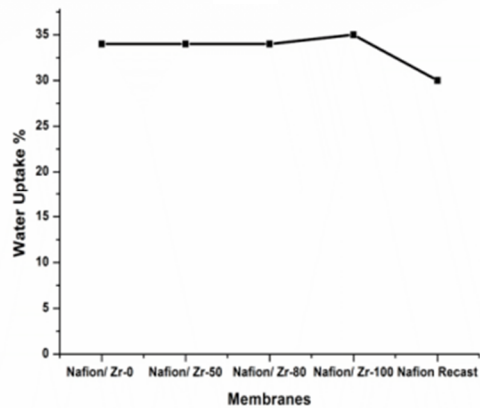


Fig. 8. Scanning Electron Microscopy (SEM).

Membrane	Water Uptake %
Nafion/ Zr-0	34
Nafion/ Zr-50	34
Nafion/ Zr-80	34
Nafion/ Zr-100	35
Nafion	30

(a)



(b)

Fig. 9. The water uptake of modified Nafion® membrane.

3. 5. Water uptake % (W_{up} %)

Figure 9(a) presents the W_{up} % of the modified and recast membrane. The results show that the modified Nafion membrane retains more water (34-35 %) by incorporating inorganic nanoparticles when comparing to the plain recast Nafion membrane (30%). It may be due to the distributed inorganic fillers on the pores of the swollen membrane which increased the hydrophilic nature of Nafion [31]. In Fig. 9(b), the graph also confirms that the modified membrane with Zr-100 has about 5% higher water-uptake than the unmodified membrane. Furthermore, zirconia nanoparticles with a higher porosity increase the water retention within the nano-composite membranes resulting also in increasing the proton conductivity due to the increase in exchange sites available per cluster which is an important parameter in fuel cells to operate at higher temperature [32].

4. Conclusions

Modified Nafion[®] membranes were analyzed using XRD, TGA, SEM techniques and their mechanical properties were characterized by the tensile test. The XRD results show that zirconia nanoparticles are well dispersed within the Nafion[®] membrane and only the monoclinic and cubic phases appears which increase the crystallinity and compatibility properties of Nafion[®] membrane. TGA results confirm the higher thermal stability of the modified Nafion[®] membrane compared to recast Nafion[®] membrane which is completely burned. The mechanical properties of the modified and recast Nafion[®] membranes show that the percentage difference of the elastic modulus of the wet and dry membranes are similar to that of the stiffness. The elastic modulus and the stiffness of dry membrane are higher than those of the wet membranes of the modified membrane. This may be due to the ZrO₂ nano-fillers enhance water affinity within the Nafion[®] membranes, promoting the ionic channels which increase in the storage modulus of the composite membrane. The results show that the modified Nafion[®] membrane can function well as electrolytes in the fuel cell.

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