The proton conductivity and mechanical properties of Nafion®/ ZrP nanocomposite membrane

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A B S T R A C T

Zirconium phosphates (ZrP) were incorporated into Nafion® 117 membrane by impregnating method to obtain a reduced methanol permeation and improved proton conductivity for fuel cell application. The mechanical properties and water uptake of Nafion® membrane incorporated with zirconium phosphates nanoparticles was more improvement when compared to the commercial Nafion® 117, due to the presence of phosphoric acid within the nanoparticles. The effect of ZrP nano filler on the membrane structural morphology and thermal properties were investigated by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermal gravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). The improved ion conductivity and decreased methanol permeability on the nanocomposite membranes showed a great potential for fuel cell applications. The nanocomposite membrane with high tensile strength was obtained due to the well dispersed zirconium phosphates within the Nafion® matrix.

1. Introduction

Fuel cell is an electrochemical device, which directly converts chemical energy into an electrical energy by using various fuels such as methanol, hydrogen, natural gas, ethanol, glucose and methylene blue in a reaction with an oxidant (oxygen). The direct methanol fuel cells (DMFCs) only utilise methanol as fuel. Nafion® reaction with an oxidant (oxygen). The direct methanol fuel cells

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the water content and proton conductivity [11]. Nanocomposite membranes shows an improvement on the tensile modulus, stiffness and exhibit better fuel cell performance than pure Nafion® 117 membrane under high temperature and low RH conditions [6]. The purpose of this work was to synthesis the modified Nafion® 117 membrane by acidic zirconia that may reduce the methanol crossover while improving the water uptake, proton conductivity and mechanical strength of membrane. The stress-strain of Nafion® 117 membrane and Nafion®/ZrP nanocomposite membrane were recorded.

2. Experimental

2.1. Materials

Phosphoric acid (Sigma), Zirconium oxychloride hydrate (Merck), Sulfuric acid (Merck), Nafion® 117 membrane (Sigma), Methanol (sigma) and hydrogen peroxide (Merck) were used as received.

2.2. Zirconia phosphates preparation (ZrP)

The zirconia phosphates (ZrP) nanoparticles was synthesised by adding 120 mL of 0.4 M ZrOCl₂·8H₂O aqueous solution in 6 M solution of phosphoric acid (H₃PO₄) and stirred for 30 min. The solution was then refluxed at 80 °C for further 24 h while stirring. The obtained material was then centrifuged and washed extensively with distilled water up to pH 3 and dried at 80 °C and then calcinated it at 600 °C for 2 h.

2.3. Synthesis of nano composite membranes (impregnation method)

Purification of Nafion® 117 membranes were done by boiling in hydrogen peroxide (3% solution) for 1hr, then boiled in sulfuric acid (0.5 M) and finally boiled in distilled water [12]. The membranes were pre-soaked in the methanol solution and 2.5wt %, 5wt % and 7.5wt % of ZrP nanoparticles were added. The soaking procedure of the membranes were repeated five times [13], and then heated at 100 °C for 2 h. The remaining solution were kept at room temperature for 24 h. The digital micrometre were used to measure the membranes thicknesses (0.18 mm). The thickness reading was taken more than 2 times in order to record the exact number.

2.4. Characterisations

The characterisations of membranes were observed under thermal gravimetric analysis (TGA), X-ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR).

2.5. Tensile test

The mechanical strength of membranes was observed under unialixial testing system. The Vernier caliper was used to measure the width, thickness and length. The 4 mm × 10 mm dimension were used in all the membranes, in order to allow the clamping area. The observed thickness of 0.18 mm was used to calculate the stress applied to the sample. The CellScale Ustretch device were used to measure membranes at 25 °C at the actuator speed of 50, 40, 30, 20 and 10 mm/min.

2.6. Water uptake ((WU)) and swelling ratio (SR)

The distilled water was used to soak membranes at the temperature of 30 °C, 60 °C and 80 °C for 24 h. After soaking the membranes was weighed in order to calculate water uptake and measured in order to calculate swelling ratio using the equations below:

\[
W_{up} = \left( \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \right) \times 100 \%
\]

\[
SR = \left( \frac{L_{\text{w}} - L_{\text{d}}}{L_{\text{d}}} \right) \times 100 \%
\]

Where \( W_{up} \) is the WU percentage, \( m_{\text{wet}} \), membrane wet mass and \( m_{\text{dry}} \), membrane dry mass, \( L_{\text{w}} \), membrane wet length and \( L_{\text{d}} \), dried length of membrane.

2.7. Ion exchange capacity (IEC)

The IEC of membranes were calculated from the titrated results and calculated using the equation below:

\[
IEC = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{m_{\text{d}}}
\]

Where \( m_{\text{d}} \) is the membrane dried mass and \( V_{\text{NaOH}} \) is the volume of titrated NaOH.

2.8. Measurements of the methanol permeability

The methanol crossover was measured with a permeation-measuring cell designed in our lab that consisted of two compartments. Compartments (A) filled with methanol solution (50 mL) and compartment (B) filled with distilled water (50 mL). The membrane was mounted between the two compartments with a diffusion area diameter of 3.5 cm. The 5M and 2M methanol solutions were used and the reading were taken at 30 °C, 60 °C and 80 °C. Methanol permeability (P) was calculated using the below equation:

\[
P = \frac{A}{V_{\text{B}}} \times C_{\text{A}} (t - t_{0})
\]

where \( C_{\text{A}}(t) \) the concentration of methanol in compartment B at diffusion time t; \( C_{\text{A}} \) is the concentration of methanol in compartment A; \( V_{\text{B}} \) the distilled water volume in compartment B; L the membrane thickness; and A is the effective permeating area.

2.9. Measurement of the proton conductivity

The membranes conductivities were measured using a four-point probe conductivity cell at 30 °C and 60 °C under 70% relative humidity (RH). The proton conductivity was observed galvanostatically at 0.1 mA current and 1MHz to 10Hz frequencies and calculated using the equation below:

\[
\sigma = \frac{L}{R_{m} A}
\]

where \( R_{m} \) is the membrane resistance obtained, A is the membrane area normal to the current flow and L is the membrane thickness.

2.10. The cell polarization and the fabrication of membrane electrode assembly

The direct methanol fuel cell (DMFC) was used to evaluate the membranes performance. The membrane electrode assembly (MEA) of anode and the cathode were consists of Pt on carbon cloth, which have been ordered from Fuel cell Store. The MEA was assembled without hot pressing. The methanol solution of 2 M was used in fuel cell testing at 60 °C. The fuel cell potential was measured galvanostatically in open air on a single fuel cell test.
3. Results and discussion

3.1. Fourier transform infrared

Fig. 1 shows the spectra of Naﬁon® 117 membrane and modiﬁed Naﬁon® membranes in the range of 400–4000 cm⁻¹. Fig. 1(a-d) shows the O–H stretching vibration at 3456 cm⁻¹, corresponding to physically adsorbed water [3, 14] and 1630 cm⁻¹ attributed to O–H bending vibration of free water molecules. Fig. 1(c & d) shows the peaks at 3456 cm⁻¹ is less shallow than commercial membrane. These can be due to the impregnated ZrP, which enhance the water content within the Naﬁon®/ZrP nanocomposite membranes. The nanocomposite membrane and commercial membrane have the peak at 1060 cm⁻¹, due to symmetric S–O stretching [15, 16], the band at 1145 cm⁻¹, due to symmetric C–F stretching and a band at 1201 cm⁻¹, due to asymmetric C–F stretching [17]. Moreover, the peaks observed at 976 cm⁻¹ attributed to the C–O–C stretching [17], the band at 512 cm⁻¹ is attributed to symmetric O–S–O bending and the band at 632 cm⁻¹ is assigned to the stretching of C–S groups [17, 18]. Furthermore, Naﬁon®/ZrP nanocomposite membranes shows that the ZrP nanoparticles was successfully impregnated, as the FTIR spectra peaks of Zr–O and P–O₄ are identiﬁed at 797 cm⁻¹, 509 cm⁻¹ and 446 cm⁻¹ [19, 20]. Fig. 1(d) also present the band at 1016 cm⁻¹ and 1550 cm⁻¹, which are attributed to bending vibrations of Zr–OH showing that zirconia nanoparticles was successfully impregnated within the nanocomposite membrane [21]. The stretch vibrations between 2925 and 2865 cm⁻¹ increases with the increase of ZrP nanoparticles, which are attributed to the C–H stretching of the modiﬁed Naﬁon® membrane as presented in Fig. 1(b-d) [22].

3.2. Scanning Electron Microscopy (SEM)

Fig. 2 shows SEM surface morphologies of the Naﬁon®/ZrP nanocomposite and Naﬁon® 117 membranes. Fig. 2(a) shows the plain Naﬁon® 117 membrane, which is dark in colour without nanoparticles. This SEM image in Fig. 2(b) shows that ZrP nanoparticles within the membrane are uniform in shape and well distributed within the membrane matrix. When 5% of ZrP is added in Naﬁon membrane, the nanoparticle is well distributed as shown in Fig. 2(c). The SEM image of Naﬁon®/7.5% ZrP nanocomposite membrane in Fig. 2(d) shows ZrP nanoparticles are agglomerated. In conclusion, the results show that, when less than 5% ZrP nanoparticles been used as nanofiller, ZrP is well
distributed within the membrane matrix and less agglomerated.

3.3. Structure analysis

Fig. 3 shows the XRD results of modified Nafton® 117 and nanocomposite membranes. Nafton® 117 membrane shows only two diffraction peaks at 17.5° and 39° 2θ as shown in Fig. 3(a), which can be attributed to semi crystalline of the perfluorocarbon chains of the ionomer [23]. The composited membranes with ZrP shows a little effect on the crystallinity, but with the lower peak height as shown in Fig. 3(b-d). Nevertheless, the incorporation of ZrP in Nafton® membrane resulted on amorphous shape and the slightly shift of 17° peak compared to the commercial membrane, as confirmed by TGA results [24]. Moreover, when ZrP weight % increase from 2.5 to 7.5 it lowers the crystallinity and the modified membrane become more amorphous.

3.4. Thermo-gravimetric analysis (TGA)

The TGA and derivative thermogravimetric (DTG) of commercial Nafton® 117 and nanocomposite membranes are shown in Fig. 4. In Fig. 4, it was observed that the membrane undergoes three weight-loss stages. At lower temperature of 100 °C the commercial Nafton® 117 membrane initial lose weight, which corresponding to the adsorption of water bonded to the sulfonic groups as shown in Fig. 4 [25]. The second weight loss starts at 380 °C, due to the sulfonic groups degradation [26]. The third weight loss was assigned to degradation of the polymer backbone chain [27]. However, Nafton®/7.5 wt% ZrP nanocomposite membrane initial lose weight at 150 °C that corresponds to the water adsorption. The second weight loss at 490 °C is due to the decomposition of the sulfonic acid groups [26]. The modified Nafton®/7.5 wt% ZrP membrane showed improved thermal degradation at high temperature of 490 °C that may be due to the nature of inorganic filler and their close interaction with the hydrophobic Nafton® backbone whereas the commercial Nafton® 117 initially decomposed at 380 °C [28]. The final weight loss around 700–900 °C was due the polymer main chain degradation [27], with 7.5% residue remain. The Nafton®/7.5%wt ZrP, Nafton®/5%wt ZrP and Nafton®/2.5%wt ZrP nanocomposite membranes showed thermal stability up to 340 whereas Nafton® 117 membrane showed a thermal stability up to 240 (DTG insert) in Fig. 4. This may be due to the water retention nanoparticles incorporated in Nafton® membrane [29], which make the suitable used in fuel cell applications. Fig. 4 (insert) showed two decomposition peaks in Nafton® and modified membranes. Fig. 4 (insert) shows that the modified Nafton® membrane with 7.5% ZrP nanoparticle obtained the highest thermal stability compared to Nafton® 117 membrane.

3.5. Tensile tests

Fig. 5 shows the stress-strain curves of the commercial Nafton® 117 membrane compared with Nafton®/2.5% ZrP, Nafton®/5% ZrP and Nafton®/7.5% ZrP nanocomposite membrane at 50, 40, 30, 20 and 10 mm/min. The stress rate of 50, 40, 30 mm/min, 20 and 10 mm/min show the elasticity and flexibility of the commercial Nafton® membrane at 0.6 stress versus strain as shown in Fig. 5(a). Fig. 5(b-c) shows that when increasing the strain rate to 50 mm/min decreases the tensile stress, whereas when the strain rate decreases to 30 mm/min increasing the

![Fig. 3. XRD patterns of (a) of Nafton® 117 membrane, (b) Nafton®/2.5% ZrP, (c) Nafton®/5% ZrP and (d) Nafton®/7.5% ZrP nanocomposite membranes.](image)

![Fig. 4. The TGA and DTG of (a) Nafton® 117 membrane, (b) Nafton®/2.5% ZrP, (c) Nafton®/5% ZrP, (d) Nafton®/7.5% ZrP nanocomposite membranes.](image)
tensile stress to 1737 kPa and 1790 kPa, respectively, this may due to the percentage of ZrP nanoparticles deposited in the membrane. The stress-strain of 10 mm/min, 20 mm/min and 40 mm/min were merely affected by varying the strain rate values, as there was no difference on their tensile strain. The engineering stress and strain were presented in the form of the graph as shown in Fig. 5. The strain rate used for testing the maximum allowable stress for Naion® varies widely from 0.08 mm/min to 50 m/s [30, 31, 32]. Furthermore, the stress-strain of the Naion®/7.5 ZrP were higher than Naion® 117 membrane at a strain rate of 50 mm/min were 1737 kPa and 947 kPa, respectively as shown in Fig. 5(d). Whereas some of the strain rate of nanocomposites membrane shows a lower strain of 3.7 and 4.9, but with a higher stress than Naion® 117 membrane. Moreover, the stress-strain of the nanocomposite membrane were higher than Naion® 117 membrane. Generally, the results showed that the modification of Naion® membrane with zirconia phosphates has improvement on the stress-strain, which is good for the membrane to withstand high stress during operation.

Fig. 5. Mechanical tensile tests results of (a) Naion® 117 membrane, (b) Naion®/2.5% ZrP, (c) Naion®/5% ZrP and (d) Naion®/7.5% ZrP nanocomposite membranes shows stress versus strain ratio curve.

Fig. 6. The methanol permeability of Naion® 117, Naion®/2.5% ZrP, Naion®/5% ZrP and Naion®/7.5% ZrP nanocomposite membranes at 5M and 2M concentration.
properties for DMFC [33]. However, the stress-strain of modified membrane with the higher percentage of ZrP nanoparticles in Fig. 5(a), is not compactible for the lower stress rate as it reduces the elasticity and mechanical properties as compared to the commercial Naﬁon® 117 membrane, which shows the elastic in the entire stress rate as shown. This can be resulted from little agglomeration of ZrP nanoparticles in the Naﬁon® matric, which introduced the brittle fracture in the modified membrane.

3.6. Methanol permeability

Fig. 6 shows the methanol permeability of Naﬁon® 117 and modiﬁed Naﬁon® membranes with 2.5% ZrP, 5% ZrP and 7.5% ZrP nanoparticles. The methanol permeability of nanocomposite membrane was lower than that of commercial Naﬁon® 117; due to ZrP added to Naﬁon® 117 that improve the barrier properties of Naﬁon® membrane towards methanol and further illustrated in Table 1. Table 1 lists the methanol permeability measured at different temperatures of 30 °C, 60 °C and 80 °C and methanol concentration of 2 M and 5 M. As observed by Yang et al., the decrease of the methanol concentration can reduce the methanol cross-over due to the decreased concentration gradient [34]. Therefore, in this study, a higher concentration of 5 M methanol solution was also used. Fig. 6 shows that the methanol permeability of Naﬁon® 117 and Naﬁon®/ZrP nanocomposite membranes measured at 60 °C were 8.84 \times 10^{-7} \text{ cm}^2/\text{s} and 0 \text{ cm}^2/\text{s} (no crossover), respectively. Fig. 6 shows that the methanol permeability of modiﬁed and unmodiﬁed Naﬁon® membranes increases as the temperature increases. The results show that Naﬁon®/ZrP nanocomposite membranes obtain a lower methanol permeation when the temperature rise to 80 °C, which indicate that there is more water permeation at high temperature than methanol. The methanol permeability for Naﬁon® 117, Naﬁon®/2.5% ZrP, Naﬁon®/5% ZrP and Naﬁon®/7.5% ZrP nanocomposite membranes are 1.99 \times 10^{-6} \text{ cm}^2/\text{s}, 1.66 \times 10^{-6} \text{ cm}^2/\text{s}, 1.55 \times 10^{-6} \text{ cm}^2/\text{s} and 1.42 \times 10^{-6} \text{ cm}^2/\text{s}, respectively as shown in Table 1. As indicated in Table 1, the modiﬁed Naﬁon® membrane with ZrP nanoparticles shows a slight decrease of methanol permeability when compared to Naﬁon® 117 membrane, due to ZrP that prevent the permeation of methanol in the membranes. The results show that the methanol permeation in the nanocomposite membranes decrease with the amount of ZrP nanoparticles added. Moreover, the modiﬁed Naﬁon® nanocomposite membranes seem to be the promising electrolytes for fuel cell application.

3.7. Water uptake, dimensional swelling ratio, Ion exchange capacity and proton conductivity measurement

The water uptake of Naﬁon® 117 membrane, Naﬁon®/2.5% ZrP, Naﬁon®/5% ZrP and Naﬁon®/7.5% ZrP nanocomposite membranes are shown in Fig. 7(a) and Table 1. Table 1 lists the water uptake and dimensional swelling ratio, Ion exchange capacity and proton conductivity of Naﬁon® 117 membranes and Naﬁon®/2.5% ZrP, Naﬁon®/5% ZrP and Naﬁon®/7.5% ZrP nanocomposite membranes. The test method was described in section

| Methanol solutions | 2M | 2M | 2M | 5M | 5M |
|--------------------|----|----|----|----|----|
| Temperature        | 30 °C | 60 °C | 80 °C | 30 °C | 60 °C | 80 °C |
| Naﬁon® 117        | -   | -   | -   | 8.84E-07 | 1.99E-06 |
| Naﬁon®/2.5% ZrP   | 0   | 0   | 0   | 0   | 0   | 1.66E-06 |
| Naﬁon®/5% ZrP     | 0   | 0   | 0   | 0   | 0   | 1.55E-06 |
| Naﬁon®/7.5% ZrP   | 0   | 0   | 0   | 0   | 0   | 1.42E-06 |

Fig. 7. Water uptake (a), linear expansion (b), Ion exchange capacity(c) and proton conductivity measurement (d) of Naﬁon® 117 membranes and Naﬁon®/2.5% ZrP, Naﬁon®/5% ZrP and Naﬁon®/7.5% ZrP nanocomposite membranes.
2.6. The Nafion®/2.5% ZrP, Nafion®/5% ZrP and Nafion®/7.5% ZrP nanocomposite membrane shows an increased in water-uptake (38%, 44% and 47%) whereas the commercial Nafion® 117 membrane obtained the lower water uptake of 32% at 60 °C as indicated in Fig. 7(a). This may be due to incorporation of nanofillers that enhanced the hydrophilic of membranes [35]. Generally, when increases the ZrP loading within Nafion® 117 membranes, it also increases the water uptake, due to the hydrophilicity of adsorption acidic materials on the membrane surface to introduce the hydrophilicity and acidity of modified membrane surface [36]. The dimensional swelling ratio at 30 °C and 60 °C shows a slightly increased with the increases in wt% of ZrP nanoparticles within the membrane as shown in Fig. 7(b). However, when Nafion®/7.5% ZrP nanocomposite membrane was soaked at higher temperature of 60 °C, a higher dimensional swelling ratio of 39% was obtained. Moreover, when temperature increases also increases the dimensional stability and water uptake of the membranes.

The proton conductivity and Ion exchange capacity (IEC) of Nafion® 117 membrane, Nafion®/2.5% ZrP, Nafion®/5% ZrP and Nafion®/7.5% ZrP nanocomposite membranes are shown in Table 2 and Fig. 7(c & d). The results in Table 2 and Fig. 7(c) shows the IEC value of Nafion® 117, Nafion®/2.5% ZrP, Nafion®/5% ZrP and Nafion®/7.5% ZrP nanocomposite membranes are 0.93 meq. g\(^{-1}\), 1.42 meq. g\(^{-1}\), 1.46 meq. g\(^{-1}\) and 1.68 meq. g\(^{-1}\), respectively. This may due to the impregnation of Nafion® membrane with ZrP, which provide the strong acid site within the membrane [36]. The IEC of the nanocomposites increases with the increases in wt% of ZrP nanoparticles within the membrane. Table 2 and Fig. 7 (d) shows that the proton conductivity of the Nafion®/7.5% ZrP and Nafion®/5% ZrP nanocomposite membranes (0.015 S cm\(^{-1}\) and 0.013 S cm\(^{-1}\)) at 30 °C were slightly lower than that of commercial Nafion® 117 membrane (2.5% ZrP) nanocomposite membranes within the membrane. The results show that introducing the zirconia phosphate nanoparticles into the membrane decreases the proton conductivity at lower temperature [37]. Whereas the water uptake of the modified Nafion® membrane was higher than unmodified Nafion® membrane as shown in Fig. 7(a). The conductivity of Nafion®/2.5% ZrP nanocomposite membrane (0.041 S cm\(^{-1}\)) at 60 °C and 70% RH, found to be higher than the commercial Nafion® membrane (0.035 S cm\(^{-1}\)), due to the increases of temperature, which increases the conductivity while also lead to the dehydration of commercial membrane shown in Table 2 and Fig. 7(d) [35, 39].

### Table 2

| Membranes        | Proton conductivity (S/cm) at 30 °C and 70% RH | Proton conductivity (S/cm) at 60 °C and 70% RH | IEC     |
|------------------|---------------------------------------------|---------------------------------------------|---------|
| Nafion® 117      | 0.015                                       | 0.035                                       | 0.93    |
| Nafion®/2.5% ZrP | 0.018                                       | 0.041                                       | 1.42    |
| Nafion®/5% ZrP   | 0.013                                       | 0.018                                       | 1.46    |
| Nafion®/7.5% ZrP | 0.011                                       | 0.012                                       | 1.68    |

3.8. Fuel cell performance

The power density and polarization curves were observed at 60 °C. The maximum power density of Nafion® 117 membrane, Nafion®/2.5% ZrP, Nafion®/5% ZrP and Nafion®/7.5% ZrP nanocomposite membranes were 112.62 mW cm\(^{-2}\), 209.71 mW cm\(^{-2}\), 206.79 mW cm\(^{-2}\) and 206.79 mW cm\(^{-2}\), respectively. The Nafion®/2.5% ZrP and Nafion®/5% ZrP nanocomposite membranes obtained a higher power density than those of Nafion® 117 membrane. These may due to the ZrP nanoparticles incorporated within the Nafion® matrix that increases the efficiency of fuel cell at 60 °C. Furthermore, the power density increases may be due to the incorporation of ZrP that suppresses the ohmic resistance of the Nafion® membrane [40]. These higher DMFC performance also confirm by the higher conductivity of Nafion®/2.5% ZrP nanocomposite membrane at 60 °C. But the slightly decrease was obtained in the performance of Nafion®/7.5% ZrP nanocomposite membrane when compared to Nafion® 117 membrane, with the power density of 112.62 mW cm\(^{-2}\) and 126.04 mW cm\(^{-2}\) at the current densities of 189 mA cm\(^{-2}\). The results show that when ZrP 7.5wt% impregnated within the membrane, as observed under TGA results resulted in agglomeration that hinders the cell performance. Therefore, Nafion® 117 membrane incorporated with 5% ZrP obtained the highest power density (145 mW cm\(^{-2}\)) than commercial membrane, with current density of 350 mA cm\(^{-2}\) as shown in Fig. 8(a). Fig. 8(b) show that the modified membrane obtained a higher voltage than commercial membrane. The Nafion®/7.5% ZrP nanocomposite membrane (0.50 V) also shows the slightly decreases in voltage at the current densities of 220 mA cm\(^{-2}\) when compared to Nafion® 117 membrane (0.58 V), Nafion®/2.5% ZrP (0.89 V) and Nafion®/5% ZrP (0.91 V) nanocomposite membranes. This may due to higher wt% of ZrP incorporated within the Nafion® matrix membrane. The lower wt% incorporation shows the improvement in the voltage and current density. This may be due to the nanoparticles that well deposited...
within the membrane pores, that are good in water retention and enhance the conductivity of modified membrane [41].

4. Conclusion

The preparation of the Nafion®/ZrP nanocomposite membrane with low methanol permeability and good proton conductivity was successfully achieved by the impregnation method. The thermal stability of the nanocomposite membrane started to decompose at high temperature of 450 °C that may be due to the nature of an inorganic filler and their close interaction with the hydrophobic Nafion® backbones. Moreover, water uptake, IEC and linear expansion of nanocomposite membrane was enhanced compared to Nafion® 117 membrane at higher temperature of 60 °C. The results show the decrease of methanol permeability of modified Nafion® membrane at higher temperature of 80 °C and 5 M methanol concentration compared to Nafion® 117 membrane. The higher temperature conductivity on the nanocomposite membranes obtained an enhanced proton conductivity than commercial Nafion® membrane, due to the addition of inorganic materials within the membranes. The lower methanol permeation and high proton conductivity resistance of modified membrane also confirmed the suitability used in fuel cell. SEM and FTIR results confirm the incorporation ZrP in the membranes that also enhanced the water uptake. The Nafion®/2.5% ZrP (209.71 mW cm⁻²) and Nafion®/5% ZrP (206.79 mW cm⁻²) nanocomposite membranes obtained a higher power density than those of commercial Nafion® 117 membranes (126.04 mW cm⁻²).

Declarations

Author contribution statement

Fulufihelo Nemavhola: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Rudzani Sigwadi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Mokhojiwa Simon Dhlamini & Touhami Mokrani: Conceived and designed the experiments.
Patrick Nonjola & Phumlani Msoni: Performed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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