Synthesis and characterization of Nafion\textsuperscript{®}-MO\textsubscript{2} (M = Zr, Si, Ti) nanocomposite membranes for higher temperature PEM fuel cells

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Abstract

Nafion\textsuperscript{®}-MO\textsubscript{2} (M = Zr, Si, Ti) nanocomposite membranes were synthesized with the goal of increasing the proton conductivity and water retention at higher temperatures and lower relative humidities (120 °C, 40% RHs) as well as to improve the thermo-mechanical properties. The sol–gel approach was utilized to incorporate inorganic oxide nanoparticles within the pores of Nafion\textsuperscript{®} membrane. The membranes synthesized by this approach were completely transparent and homogeneous as compared to membranes prepared by alternate casting methods which are cloudy due to the larger particle size. At 90 °C and 120 °C, all Nafion\textsuperscript{®}-MO\textsubscript{2} sol–gel composites exhibited higher water sorption than Nafion\textsuperscript{®} membrane. However, at 90 °C and 120 °C, the conductivity was enhanced in only Nafion\textsuperscript{®}-ZrO\textsubscript{2} sol–gel composite with a 10% enhancement at 40% RH over Nafion\textsuperscript{®}. This can be attributed to the increase in acidity of zirconia based sol–gel membranes shown by a decrease in equivalent weight in comparison to other nanocomposites based on Ti and Si. In addition, the TGA and DMA analyses showed improvement in degradation and glass transition temperature for nanocomposite membranes over Nafion\textsuperscript{®}.

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1. Introduction

In recent years, there have been extensive research efforts in the development of newer proton conducting membranes for higher temperature proton-exchange membrane (PEM) fuel cell\cite{1,2}. Nafion\textsuperscript{®}, the conventional proton conducting polymer electrolyte membrane is expensive, mechanically unstable at temperatures above 100 °C, and conductive only when soaked in water, which limits fuel cell operating temperatures to 80 °C, which in turn results in lower fuel cell performance due to slower electrode kinetics and low CO tolerance\cite{3}. The operation of fuel cells at higher temperature possesses many system advantages such as smaller heat exchangers, and easier integration with reformers. Thus, the development of membranes which are mechanically and chemically stable at higher temperatures (above 100 °C) is an active area of research for producing economical fuel cells.

The efforts to develop these higher temperature membranes include modification of the conventional host polymers, e.g., via incorporation of various hygroscopic inorganic nanosized particles or by developing alternate new polymer systems\cite{4–17}. Malhotra and Datta first proposed the incorporation of inorganic solid acids in the conventional polymeric ion-exchange membranes such as Nafion\textsuperscript{®} with the objective of serving the dual functions of improving water retention as well as providing additional acidic sites\cite{4}. Thus, they doped Nafion\textsuperscript{®} membranes with heteropolyacids, e.g., phosphotungstic acid (PTA), and were able to show high fuel cell performance at lower RH and elevated temperature (120 °C). Unfortunately, due to high water solubility, the PTA eventually leaches out from the PEM. Ramani et al. have more recently shown that Nafion\textsuperscript{®}-PTA membranes can be stabilized by heat treatment and the leaching of PTA can be reduced\cite{5}. Nafion\textsuperscript{®} can also be modified by the incorporation of hygroscopic oxides such as SiO\textsubscript{2} and TiO\textsubscript{2} to increase water uptake\cite{6}, or inorganic solid acids such as ZrO\textsubscript{2}/SO\textsubscript{4}\textsuperscript{2–}\cite{18}.
Watanabe et al. modified Nafion® PEMs by the incorporation of nano-sized particles of SiO₂, TiO₂, Pt, Pt–SiO₂ and Pt–TiO₂ to decrease the humidification requirements of PEMFCs. When operated at 80 °C under low humidification, the modified PEMs showed lower resistance than Nafion®. This improvement was attributed to the suppression of H₂ cross over by in situ Pt along with the subsequent sorption of the water produced on the incorporated oxides. Adjemian et al. introduced nano-sized SiO₂ into Nafion® pores and tested various thickness and EW membranes [8]. The benefit of these composite membranes appears to be in stable operation versus conventional Nafion® at a cell temperature of 130 °C due to higher rigidity, when both were tested under fully humidified conditions. The investigators noted that the unmodified PEMs showed thermal degradation, while the SiO₂ modified PEMs did not show such damage. Costamagna et al. incorporated zirconium phosphate into a Nafion® membrane and the results obtained were similar [11]. Zaidi et al. embedded heteropolyacids to different extents in sulfonated polyether ether ketone (S-PEEK) [12]. The highest performing composite was a tungstophosphoric acid doped, 80% sulfonated PEEK PEM. It showed conductivity similar to that of Nafion®. Adjemian et al. have also synthesized Nafion® PEMs containing silicon oxide, as well as zirconium phosphate particles [14]. They found that silicon oxide modified membranes exhibited better robustness and water retention and better performance. Similarly, Staiti et al. have also investigated Nafion-silica membranes doped with phosphotungstic acid and silicotungstic acid for direct methanol fuel cell operation at 145 °C [15]. Tazi and Savadogo have prepared membranes based on Nafion®, silicotungstic acid and thiophene [16]. These modified membrane had better water retention and thermomechanical properties. On the other hand, Arico et al. reported higher proton conductivity of inorganic acid doped composite membranes such as Nafion®/SiO₂ and Nafion®/SiO₂/PWA + SiO₂ over all the temperature range of experiments [17]. Other examples of polymer/inorganic composite membranes include Nafion®/Al₂O₃, Nafion®/ZrO₂, Nafion®/ZrP, Nafion®/PTA, Nafion®/Zeolite, SPEEK/ZrO₂, SPEEK/ZrP, SPEEK/ZrO₂/PTA, and PBI/(SWA + SiO₂), etc.

Based on this work accomplished on higher temperature membranes, it can be concluded that the approach of synthesizing nanocomposite membranes either by casting a bulk mixture of powder or colloidal state of inorganics with a polymer solution, or in-situ formation of inorganic particles utilizing the membrane as template [13], is very promising. The advantage of in-situ method is that the particle size can be controlled by the concentration of precursors because the size and dispersion of these solid particles are of utmost importance in final performance of fuel cells. Mostly, the in-situ methods are based on sol–gel reactions between the organo metallic compound as the precursor and water within the pores of the membrane. Though these membranes show better water sorption and proton conduction properties, better mechanical properties with higher fuel cell performance and long term stability are yet to be established.

In our earlier work, we have shown the potential of preparing nanocomposite membranes using sol–gel chemistry with improved hydration as well as conductivity at higher temperature and lower RH conditions [18]. In addition, we have developed a theoretical model for proton transport in Nafion® and in nanocomposite membranes based on the parallel pore model incorporating various proton transport mechanisms such as surface proton hopping, Grotthuss diffusion, and traditional en masse diffusions [19,31]. This allows an understanding of the contributions from various proton transport mechanism in nanocomposite membranes and the effect of the inorganic additives for designing new PEMs.

In the present work, we synthesized Nafion®/ZrO₂, Nafion®/SiO₂ and Nafion®/TiO₂ nanocomposite membranes via in situ sol–gel technique and compared with unmodified Nafion® in terms of water uptake, proton conductivity at different relative humidity conditions (RHs), fuel cell performance, and ion exchange measurements. These nanocomposite membranes were further characterized using TGA (thermo gravimetric analysis) and DMA (dynamic mechanical analysis) to determine degradation and glass transition temperatures (Tg).

2. Experimental

2.1. Membrane preparation

The method of preparation of the ZrO₂, SiO₂ and TiO₂ composite PEMs was based on the in situ sol–gel synthesis methods [13]. In this procedure, the host PEM serves as a template that directs the morphology, particle growth, and size of the oxide in the PEM matrix, resulting in nano-sized particles. As received Nafion® membranes (Sigma-Aldrich Corp., St. Louis, MO) were boiled in 3 wt.% H₂O₂ for 1 h and then rinsed in water. They were then immersed in 1 M NaOH solution and heated for 6 h to convert the membrane to Na⁺ form. This ensures good mechanical strength of Nafion® membrane for withstanding the subsequent processing steps. Then the membrane was rinsed in DI water at 60 °C for 30 min [21–22].

The purified Na⁺ form membranes were then placed in a vacuum oven and heat treated at 110 °C for 12 h. The membranes were then immersed in 10:1 ethanol/H₂O solution for an hour. The ethanol/H₂O mixture served to further swell the pores of the PEM to maximize the absorption of the precursor solution. The membranes were removed and immersed in 0.5 M 70 wt.% Zirconium (IV) propoxide solution (obtained from Aldrich) for 6 h and then rinsed in acetone in order to remove surface ZrO₂. The membranes were then removed and heated at 110 °C in vacuum for 24 h to complete the condensation reactions. After this the membranes were boiled in 50 vol.% H₂SO₄: H₂O solution for 6 h for sulfation. This nanocomposite PEM is denoted here as “Nafion®-
Fig. 1. SEM images of membranes synthesized by both the in situ and doping methods. (a) Nafion®-ZrO₂ doped membrane. (b) The Nafion®-ZrO₂ sol–gel PEM is homogeneous and transparent demonstrating no phase separation.

Using a similar protocol, Titanium(IV) tert-butoxide and Tetraethyl orthosilicate (TEOS) were utilized as the precursors utilized to synthesize “Nafion®-TiO₂ sol–gel” and “Nafion®-SiO₂ sol–gel” membranes, respectively.

The membranes synthesized by this method were completely transparent and homogenous as compared to membranes prepared by our previous casting methods [18], which were cloudy due to presence of much larger particles. Fig. 1 shows scanning electron microscope (Amray Model 1610 Turbo SEM) images for the membranes prepared by both methods. The membrane prepared using the casting method had larger zirconia particles with size ranging in 5–15 μm. On the other hand, the sol–gel membranes showed no X-ray scattering. Also the surface of sol–gel membranes did not show any deposition of oxides which confirms that the zirconia is present within the pores of Nafion® membrane. Similar observations were made for other nanocomposite membranes synthesized using the sol–gel method.

2.2. Water uptake measurements

The tapered element oscillating microbalance (TEOM® Series 1500 PMA Reaction Kinetics Analyzer, Rupprecht & Patashnick Co. Inc. Albany NY) was utilized to measure the water uptake of the composite PEMs as compared to unmodified Nafion® membrane [20–21]. The sample mass change in TEOM was measured as the frequency change of the tapered element oscillatory bed as described by us earlier [20]. The RH was controlled by mixing metered flows of a wet (saturated with H₂O) and a dry helium stream. Calibration was done with a RH meter (FH A646-R, ALMEMO, Alhborn, Munich, Germany). The membrane was cut into thin strips (1.5 mm x 1.5 mm) and packed carefully along with quartz wool into the oscillating test bed of the TEOM® to avoid rattling. The water uptake was measured for all samples at 90 °C from 0 to 90% RH, and at 120 °C from 0 to 40% RH. After the sample was loaded, it was exposed to the helium gas having the desired RH, and the real-time mass change was observed to determine when the equilibrium amount of water had been adsorbed onto the membrane. The working principle and data collection procedures are also explained elsewhere [23–24].

2.3. Ion-exchange capacity measurements

A 0.2 g sample of the composite PEM was exchanged with NH₄⁺ by immersing the sample in 1 M ammonium acetate for 24 h and then in ammonium chloride for an additional hour. The PEM was then washed with DI water to remove any excess NH₄⁺ ions. To ensure that all excess NH₄⁺ had been removed, a drop of 1 M silver nitrate was added to the wash. If NH₄⁺ ions were present, a white precipitate would form. The PEM was then stored in 50 ml DI water. Adding 2 ml of 5 M NaOH solution to the sample, caused the subsequent exchange of NH₄⁺ with Na⁺. Utilizing a calibrated ammonia electrode (Model 95-12 ORION, Boston MA), the amount of NH₄⁺ released could be accurately quantified thus providing an accurate measure of the ion-exchange capacity [25].

2.4. Ex situ conductivity testing

The conductivity measurements were made with a perturbation voltage of 10 mV in the frequency range 0.01–10⁶ Hz using a Solartron SI 1260 FRA (Solartron, Hampshire, UK). Both real and imaginary components of the impedance were measured and the real z-axis intercept was assumed to provide the membrane resistance, and hence, conductivity. A composite membrane sample was sandwiched between two electrodes each on either side to measure the conductivity, similar to the procedure reported in literature and then placed in humidity controlled chamber [26]. The humidity of the chamber was monitored utilizing a dew point/temperature probe (HMP 238, Vaisala, Woburn, MA). An air stream was saturated with water by bubbling through a humidifier. This wet stream was heat-traced to the chamber to avoid condensation.
The chamber and the humidifier were both heated to 90 and 120 °C, respectively, to obtain the desired partial pressure of water. The conductivity of the PEM was measured at 90 °C in the RH range from 10 to 90%, while at 120 °C the RH range was from 10 to 40% to simulate dry conditions. These conditions are the same as those utilized for the water uptake measurements.

2.5. MEA testing

The electrodes utilized are commercially available from E-TEK (Somerset, NJ). The type selected was the single-sided ELAT® gas-diffusion electrode (20% Pt-on-C, 0.35–0.4 mg Pt/cm²). The active layer of electrode was brushed with 5% Nafion® solution (0.6–0.8 mg/cm² MEA). This electrode was placed on either side of the PEM and the resulting membrane-electrode assembly (MEA) placed in a hot press. The temperature of the hot press was then raised to 130 °C and a pressure of 272 atm was applied for 120 s. The MEA thus prepared was mounted in a 5 cm² fuel cell test fixture, obtained from Fuel Cell Technologies (Los Alamos, NM). The cell was fed with humidified H₂ and O₂ supplied at pressure 1 atm using electronic mass flow controllers (MKS Model No. 1179A22CS1BV-S; Andover, MA) and was controlled by the electronic load (Series 890B Fuel Cell Test System, Scribner Associates Inc. Southern Pines, NC). Utilizing software (Fuel Cell Test Software Version 2.0, Scribner Associates, Inc.), the mass flow rate of the feed gas was programmed to stoichiometry dependent flow rates. The load has an inbuilt feature of measuring in situ MEA ohmic resistance utilizing the current interruption method. The pressure of the reactant gases was monitored using pressure gauges (Matheson, Model No. 63-5612). The startup procedure involved bringing the humidifier temperature up to a set value of 80 °C, then increasing the fuel cell to 80 °C and operating with 1 atm H₂ and O₂ at current controlled mass flow rates. The load was cycled for additional 6 h and then a constant voltage polarization curve was taken. Thereupon, another 12 h of break-in period was utilized and then a final polarization curve was obtained as follows. The voltage was set at 0.6 V set for 30 min and then data were taken every 6 s for 15 min. Similar procedure was repeated for other voltage conditions. The data were collected every 6 s for 15 min at each voltage set-point.

3. Results and discussion

3.1. Water uptake measurements

Figs. 2 and 3 show the water uptake measurements for the nanocomposite membranes at 90 and 120 °C, respectively. At both temperatures, all Nafion®-MO₂ nanocomposite exhibited better water uptake at a given relative humidity (RH) than unmodified Nafion® membrane. Nafion®-ZrO₂ nanocomposite demonstrated about 33% and 45% higher water uptake at 90 and 120 °C respectively at water activity of 0.4 as compared to Nafion® membrane. Similarly, titania

Dynamic mechanical analysis (DMA) was also employed to determine glass transition temperature for the nanocomposite membranes using Thermal Analysis 2980 DMA in a temperature range 25–175 °C. For viscoelastic materials, like Nafion®, stress consists of elastic and a viscous component. The elastic component or storage modulus, accounts for how the material behaves like an ideal solid and the viscous component or loss modulus, accounts for how the material behaves like an ideal fluid. The phase angle shift between stress and strain is represented by δ, which varies between 0 (100% elastic) and 90 (100% viscous) [29–30].

\[
\frac{E''}{E'} = \tan(\delta)
\]  

where \( E' \) is storage modulus (elastic component) and \( E'' \) is loss modulus (viscous component) of the material.

The glass transition temperature (\( T_g \)) of a material can be taken as either the peak of the loss modulus versus temperature curve or the peak of the tan(δ) versus temperature curve. In the present work, \( T_g \) is obtained from the peak of tan(δ) versus temperature data.

3.2. Thermo-mechanical characterization

The morphology of the synthesized nanocomposite membranes was investigated using scanning electron microscope (Amray Model 1610 Turbo SEM).

Thermogravimetry analysis (TGA) of the nanocomposite membranes was accomplished on a TGA TA Instruments 2050 system in a temperature range 25 to 700 °C at the heating rate 20 °C/min. A known mass of sample was placed into the analyzer and was heated at a constant rate so that the entire polymer eventually volatilizes.
based membranes showed about 20–25% higher water uptake than Nafion® at the temperatures of interest. Silica membrane showed water uptake similar to Nafion® at 90°C, and about 15% higher than Nafion® at 120°C. The enhanced water uptake can be attributed to the hydrophilic nature of the acidic inorganic additives within the pores of Nafion® membrane and the increased acidity and surface areas of nanoparticles. The basic sorption trend at both temperatures was similar, with water uptake increasing from silica to titania to zirconia nanocomposites. This is in order of increasing acid strength. From the results obtained, it can be concluded that incorporation of nanosized acidic inorganics with higher surface areas, enhances water uptake properties of Nafion® membrane, which is a key design objective for high temperature membranes. The advantage of inorganic additives in PEMs is more evident more at higher temperatures and lower RHs. Higher water uptake and enhanced acidity result in greater proton conductivity, which would presumably result into better fuel cell performance under hot and dry conditions. Also, the sorption isotherm shape obtained for nanocomposite membranes were found to be similar to that of Nafion®, with lower water uptake at low RHs and then sharp increase in the amounts of water uptake after water activity of 0.6. Hence, the basic mechanism of water sorption must be similar for all nanocomposite membranes. The difference is due to the change in acidity and active surface area of membrane.

3.2. Ion exchange capacity

Table 1 lists the experimental EW measured for all the nanocomposite membranes. It was observed that Nafion®-ZrO_2 sol–gel was the most acidic membrane, having the lowest EW of about 1020 ± 10. Hence, as observed from Figs. 2 and 3, this membrane exhibited highest water uptake, as compared to other nanocomposite membranes, which had higher EW as shown in Table 1. Hence, the ion exchange measurements are in agreement with the water uptake results, and also due to the fact the sulfated zirconia is more acidic than other additives.

3.3. Conductivity measurements

Figs. 4 and 5 show the conductivity measurements for the nanocomposite membranes at 90°C and 120°C, respectively,
as compared to Nafion® membrane. At both temperatures, Nafion®-ZrO\textsubscript{2} sol–gel nanocomposite showed higher conductivity than Nafion® for over the complete range of water activity. At 90 °C, both titania and silica nanocomposites showed somewhat lower conductivity than Nafion®, while zirconia membranes had a sharp increase in conductivity at water activity of 0.7. At 120 °C, Nafion®-SiO\textsubscript{2} sol–gel nanocomposites exhibited lower conductivity than Nafion®, while zirconia membranes showed about 8–10% higher conductivity.

The increase in the conductivity of Nafion®-ZrO\textsubscript{2} sol–gel nanocomposites is the combined result of higher water uptake as well as acidity. Although other nanocomposites demonstrated higher water uptake, they showed about similar acidity and lower conductivity than Nafion®. Hence, from water uptake, ion exchange capacity and conductivity results, it is evident that higher water uptake does not inevitably result into higher conductivity. As described in our modeling analysis, it is not only the total water uptake, but also the distribution of water between surface and bulk that determines conductivity [19]. Bulk water is much more effective in proton conduction.

3.4. Thermo-mechanical analysis

The TGA thermograms of the nanocomposites are displayed in Fig. 6 as compared to Nafion® membrane. From the Fig. 6, it is observed that all the membranes retain more than 90% of their weight up to a temperature of about 310 °C. Above 310 °C, all the membranes started to decompose and lose weight quite rapidly. This decomposition behavior can be attributed to the loosening of sulfonic acid groups present in the unmodified Nafion® membrane [27]. However, it was observed that the temperature at which this decomposition occurs shifts with the nature of inorganic additive within the pores of Nafion® membrane. For example, sharp thermal degradation of the unmodified Nafion® occurs at about 325 °C, whereas, for Nafion®-ZrO\textsubscript{2} and Nafion®-SiO\textsubscript{2} sol–gel membranes degradation temperature shifts to about 360 and 470 °C, respectively. The TiO\textsubscript{2} membranes showed not much improvement in thermal degradation temperature as compared with Nafion. Deng et al. also reported an initial increase in the degradation temperature, when SiO\textsubscript{2} was added into Nafion® membrane [28]. We observed similar increment for ZrO\textsubscript{2} nanocomposite membrane. Since the inorganic particles were in nanosized range, the increment in the decomposition temperature could be due to cross-linking of these inorganic additives frameworks in the nanocomposite membranes. A systematic investigation of the TGA behavior of these additives would give more insights for the trends observed. Also, the weight of the inorganic residue left after the TGA runs exhibited that these nanocomposites have 3–4 wt. % of inorganics within the pores of Nafion membrane.

The DMA thermogram for nanocomposite membranes along with unmodified Nafion® membrane is shown Fig. 7. For all membranes, \( T_g \) was obtained from the peak of tan (δ). It can be seen that the \( T_g \) for all the nanocomposite membrane shifts to higher temperatures. From the literature, it is known that above 115 °C the network of hydrophilic clusters, made up from the sulfonic groups, is becoming extremely mobile, before the clustered structure finally collapses [29–30]. This can be either due to loss of water under dry and hot conditions, or further uptake of solvents if exposed to saturated solvent/water vapor. This high mobility of the backbone and cluster network is shown by high value of loss tangent for unmodified Nafion® membrane, reaching values of 0.62 as shown in Fig. 7.

Further, we see that the \( T_g \) increases for the nanocomposites, which implies that they are thermo-mechanically more stable than unmodified Nafion® membrane. For instance, the \( T_g \) for Nafion®-112 membrane was found to be around 110 °C, whereas, for Nafion®-SiO\textsubscript{2}, Nafion®-TiO\textsubscript{2} and Nafion®-ZrO\textsubscript{2} sol–gel membranes temperature shifts to about 118, 122 and 142 °C, respectively. The peak loss tangent values decreases from 0.62 for Nafion® to 0.52.
Fig. 8. The cell performance of Nafion® 112 MEA vs. Nafion®-MO 2 sol–gel, composite MEA. Oxygen and H2 at 2.0 and 1.3 times stoichiometry flows, respectively, \( P = 1.0 \text{ atm, } T_{\text{Humidifier}} = 80 \degree \text{C, } T_{\text{Cell}} = 80 \degree \text{C.} \)

for Nafion®-ZrO 2 sol–gel membranes. The membrane thus becomes more elastic in nature and can withstand higher temperatures due to the presence of the inorganic additives within the pores of unmodified Nafion® membrane. These results are also in agreement with the TGA thermograms, which show increase in the degradation temperatures for the nanocomposite membranes.

Thus, the results obtained from TGA and DSC shows the improved potential of the nanocomposite membranes for higher temperature operations for fuel cells applications. Although, all the nanocomposite membranes exhibit better thermo-mechanical properties than Nafion® membrane, the stability of the nanocomposite membranes needs to be tested in PEMFC system.

3.5. MEA measurements

The fuel cell performance of a single cell with all four types of membranes under fully humidified conditions at 80 °C is shown in Fig. 8 and under dry conditions \( T_{\text{Cell}}: 110 \degree \text{C, } T_{\text{Humidifier}}: 80 \degree \text{C} \) in Fig. 9. Fig. 10 shows the fuel cell performance for Nafion-ZrO 2 nanocomposite membrane at \( T_{\text{Cell}}: 135 \degree \text{C and } T_{\text{Humidifier}}: 80 \text{ and } 90 \degree \text{C.} \) Lower EW implies higher acidity of composite membranes. Since sulfated zirconia is acidic, it causes higher water sorption in the nanocomposites. Our recent modeling paper [31] predicts the conductivity of the in situ sol–gel prepared Nafion®-ZrO 2 nanocomposite membranes accurately as a function of relative humidity without any fitted parameters. Nafion®-ZrO 2 nanocomposite membrane showed higher proton conductivity compared to Nafion® at the same temperature and humidity conditions due to the improved water uptake, provision of strong acid sites and higher bulk to surface water ratio, which is critical for higher proton conductivity. Hence, there is slight improvement in performance of fuel cell at 80 °C for Nafion®-ZrO 2 sol–gel nanocomposite as compared to other membranes. However, Nafion®-SiO 2 exhibited subsequently lower performance than Nafion® as contrary to results reported in literature. The reason for poor performance for SiO 2 membranes may be attributed to lower conductivity of SiO 2 membrane and higher EW as compared to Nafion® membrane. At 110 °C, both TiO 2 and ZrO 2 membranes have about 30–40 mA/cm 2 higher current at 0.5 V compared to Nafion® membranes, while SiO 2 membranes had similar performance to Nafion®. At 135 °C, we obtained current densities for ZrO 2 membranes under hot and dry conditions. These results suggest that there is a potential for improvement in fuel cell performance using sol–gel nanocomposites.
Under the test conditions, the in situ conductivity for nanocomposite membranes, measured using current interrupt methods, was higher than that of Nafion®. Further, it is possible that the membrane-electrode interface has undergone morphological change under hot and dry conditions. The conventional catalyst layer is still unmodified with nanocomposite membrane, which on modification could considerably further improve the performance. Hence, our future work would focus on optimizing the catalyst structure including incorporating sol–gel nanocomposite within the catalyst layer to increase its conductivity under hot and dry conditions. This would eventually, lead to the development of stable composite membrane electrode assemblies that perform better and are more durable under higher temperatures and lower RH.

4. Conclusions

Nanocomposite Nafion®(M02 (M = Zr, Si, Ti) membranes were synthesized by in situ sol–gel method and characterized for high temperature operation of PEM fuel cells. Nafion®-ZrO2 sol–gel membranes, especially, demonstrated higher water uptake and conductivity than unmodified Nafion® membranes. Also, Nafion®-MO2 (M = Si, Ti) showed good water uptake properties. Further, all the nanocomposites exhibited better thermomechanical properties than Nafion®. The degradation temperatures and Tg improved for all nanocomposites. This shows that these membranes are tolerant to high temperature above 120 °C, which is a design goal of this work. Thus, both chemical and physical properties were modified by incorporating nanosized inorganic additives having higher acidity and water uptake properties. The membranes synthesized by sol–gel methods were also very homogeneous.

The future work includes testing the long term durability of these nanocomposite membranes. Since Nafion®-ZrO2 membranes exhibited better water sorption and acidity, our focus is also to characterize the electrode catalyst layer by incorporating the sol–gel membrane. This might enable us to address the issue of loss of active electrochemical surface area at higher temperatures. The understanding developed could result into stable composite membrane electrode assemblies (CMEAs) for fuel cell commercialization.

References