

Synthesis and characterization of cross-linked chitosan membranes for application as alternative proton exchange membrane materials in fuel cells

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Abstract

Chitosan membranes cross-linked in sulfuric acid are evaluated for their thermal stability, water absorption and proton conductivity properties as alternative proton exchange membrane (PEM) material for application in fuel cells. Chitosan membranes are found to be more hydrophilic than Nafion 117 in water uptake experiments. Chitosan membranes absorb about 60% water on average compared with about 30% for Nafion 117. Preliminary TGA/DSC thermal stability studies show that after the initial weight loss due to water, chitosan membranes decompose in three stages with the final stage beginning at about 300 °C.

Chitosan membrane proton conductivities under various temperature and humidity conditions are reported and compared with that for the commercial membrane Nafion 117. Partially-hydrated chitosan membranes at ambient temperature display a proton conductivity of about 0.005 S cm⁻¹ as opposed to 0.08 S cm⁻¹ for Nafion 117 under the same conditions. At 60 °C (full hydration) Nafion 117 membranes have a conductivity of about 0.12 S cm⁻¹ and chitosan membranes have 0.02 S cm⁻¹.

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1. Introduction

Proton exchange membrane (PEM) material is used in fuel cells. This important component is also known as a polymer electrolyte membrane (PEM) or a solid polymer electrolyte (SPE). The membrane serves to separate the reactant gases, provide the electrolyte for energy-generating electrochemistry, and to facilitate the selective transport of protons from the anode to the cathode.

Polymer electrolyte membranes are somewhat unusual electrolytes in that, in the presence of water, which is readily absorbed by the membranes, the negative ions are rigidly held within the structure. Only the positive ions contained within the membranes are mobile and are free to carry positive charge through the membrane. In polymer electrolyte membrane fuel cells (PEMFCs), these positive ions are hydrogen ions, or protons, hence the term: 'proton exchange

membrane'. Movement of the hydrogen ions through the membrane, in one direction only, from anode to cathode, is essential to fuel-cell operation. Without this movement of ionic charge within the fuel cell no current will flow in the external circuit. The use of a solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolytes.

The requirements for proton-conducting polymer electrolyte membranes are generally agreed to include the following:

- low cost;
- high proton conductivity;
- good fuel barrier properties (minimal gas or methanol cross-over);
- high mechanical strength;
- thermal and chemical stability;
- electronically non-conducting.

The state-of-the-art proton exchange membrane is a polymer commercially called Nafion[®] that was developed by DuPont de Nemours, USA, in the 1960s. The Nafion mem-

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brane is comprised of a perfluorinated backbone with side chains that are terminated by strongly acid SO_3H groups. Nafion has almost all of the necessary properties for a good fuel-cell membrane. The most significant drawbacks are the relatively high cost, the dependence on water for conduction, and instability at temperatures in excess of 100°C . The last mentioned is particularly unfortunate because membranes that allow stable, high-performance operation at elevated temperature should lead to substantial improvements in fuel-cell performance.

As a natural polymer, chitosan is one of the promising membrane materials and has been studied widely. It is inert, hydrophilic, and insoluble in water, alkali and organic solvents. Its solubility in dilute organic acids allows for gel formation in various configurations, membranes included. Chitosan has been studied as membrane material for ultrafiltration, reverse osmosis, pervaporation, and lithium batteries [1]. Chitosan is the *N*-deacetylated derivative of chitin, which is a naturally abundant polysaccharide and the supporting material of crustaceans, insects, etc. Chitin is easily obtained from crabs or shrimp shells and fungal mycelia. The removal of proteins in chitin by heat treatment causes its deacetylation, simultaneously.

In its normal state, a chitosan film has very low electrical conductivity. Although the structure of a chitosan monomer has three hydrogen atoms, they are strongly bonded to the structure and cannot be mobilized under the action of an electric field to give a proton conductor. It has been found, however, that if chitosan is dissolved in acetic acid and the resulting solution is cast into a thin film, then the H^+ or H_3O^+ and CH_3COO^- ions in the acetylated chitosan film will be dispersed in the immobilized chitosan solvent and these ions can be mobilized under the influence of an electric field. If H^+ or H_3O^+ ions are more mobile than the CH_3COO^- ions the film becomes a proton conductor. Chitosan in an acidic medium can become a polyelectrolyte through the protonation of the $-\text{NH}_2$ groups [2].

Ionically conducting chitosan membranes have been synthesized and used as material for the fabrication of solid polymer batteries [3]. For application as proton exchange membranes for fuel cells, the chitosan membranes will have to be cross-linked in order to ensure physical and chemical stability in the presence of water.

2. Experimental

2.1. Chitosan membrane synthesis and fabrication

Chitosan membranes were fabricated from medium molecular weight (MMW) chitosan. The following chemicals and materials used for the synthesis of chitosan membranes were supplied by Sigma–Aldrich:

- medium molecular weight (MMW) chitosan;
- sodium hydroxide solution (2 M);

- sulfuric acid (98%);
- acetic acid.

The chitosan membranes were prepared by the following procedure: 1 g of chitosan flakes was dissolved in 100 ml of 1 wt.% acetic acid solution. After complete dissolution of the chitosan flakes, the solution was filtered and cast on glass plates and left to dry via evaporation for 24 h. The drying membranes were then transferred to an oven and dried at 60°C for 6 h. The dried membranes were neutralized in 2 M NaOH for 5 min and thoroughly washed. The membranes were later cross-linked and protonated by submersion in 0.5 M H_2SO_4 for 24 h. They were then washed and stored in de-ionized water at ambient temperature. This synthesis method for chitosan membrane has been reported by Ge et al. [4], who found that the optimum condition for ionic cross-linking of the membranes was 0.5 M H_2SO_4 at ambient temperature. The membrane thickness was adjusted by varying the amount of solution cast on a glass plate with the same surface area. The membrane thickness was determined using a Mitutoyo Digital micrometer.

The chemical structure of chitosan membrane cross-linked in sulfuric acid is shown in Fig. 1. The amino groups in chitosan and sulfate ions have a coulombic interaction. Therefore, they cross-link the main chains of the chitosan ionically as shown below.

2.2. Water uptake measurements

Synthesized chitosan membranes were cut and stored in an equilibration bottle. To determine the water uptake at each state of hydration, the membranes were removed from the equilibration bottles, blotted dry using a tissue paper to remove excess surface water, and quickly weighed to give the initial wet weight. The membranes were then dried using the following drying procedures:

Procedure 1: dried at room temperature under vacuum for 15 h;

Procedure 2: dried under vacuum at room temperature for 15 h followed by 1 h at 105°C ;

Procedure 3: dried for 7 days over P_2O_5 in a desiccator;

Procedure 4: dried over P_2O_5 for 7 days in a desiccator followed by 1 h of heat treatment at 105°C under vacuum.

After drying, the membranes were rehydrated by immersion in liquid water at three different temperatures (27 , 65 and 100°C) for 1 h and weighed immediately after wiping off the surface water.

The percentage water uptake was calculated using the following expression:

$$\text{water uptake (\%)} = \frac{m_1 - m_2}{m_2} \times 100 \quad (1)$$

where m_1 is the membrane sample wet weight upon rehydration and m_2 represents the weight of the dry membrane sample.

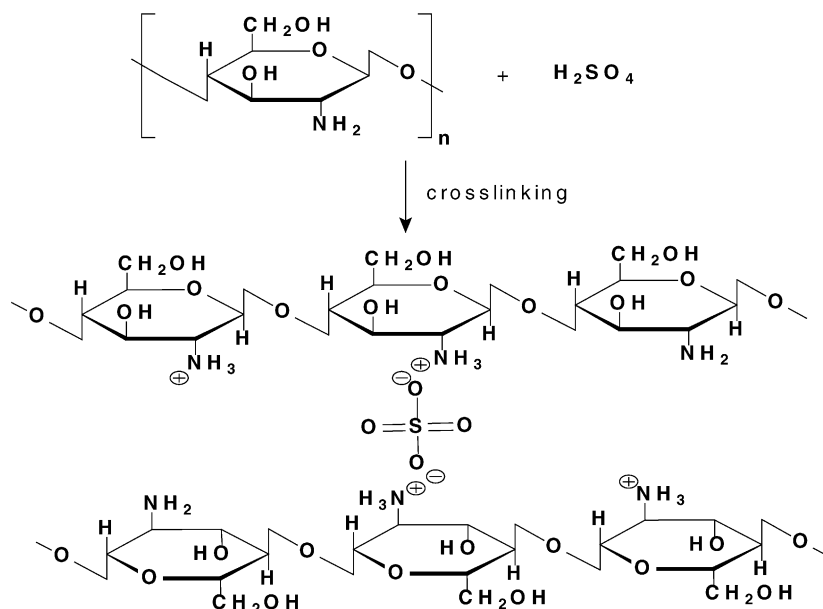


Fig. 1. Chemical structure of ionically cross-linked chitosan. The amino groups in chitosan and sulfate ions have a coulombic interaction which makes possible the ionic crossing of the main chains.

2.3. Thermal stability measurements

A single thermo-analytical technique is seldom adequate to characterize sufficiently a property such as thermal stability or thermal decomposition. It is common and advisable, therefore, to use more than one thermal method and even other analytical techniques in a thermal stability investigation. In the present study of chitosan membrane thermal stability, two complimentary methods were employed, namely, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2.3.1. Thermogravimetric analysis (TGA)

Small disks of Nafion 117 and chitosan membranes (8 mm diameter each) were punched out to fit aluminum sample pans. The membrane samples were dried over P_2O_5 in a desiccator before placing them in a TA Instruments TGA 2050 instrument for thermal analysis at a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 600°C . To ensure complete decomposition of the chitosan membranes, the samples were sometimes heated to 800°C . All the samples were analyzed in both air and nitrogen at a flow rate of $25\text{ cm}^3\text{ min}^{-1}$. Both gases were supplied by Afrox. The first derivative of mass-change with respect to time (dm/dt , called derivative thermogravimetry (DTG)) was calculated and plotted as a function of temperature. Using DTG analysis, a series of peaks were obtained instead of stepwise TG curves. The areas under the peaks are proportional to the total mass-change of the membrane sample. The DTG is more precise in showing the onset of a reaction that is accompanied by mass loss and also permits the reaction temperatures to be defined more precisely.

2.3.2. Differential scanning calorimetry (DSC)

Membrane samples for DSC analysis were cut and weighed on a microbalance and encapsulated in hermetically-sealed aluminum pans. Samples that weighed 9 mg on average were used. The samples and reference were placed in a TA Instruments DSC 2010 instrument and scanned at $10^\circ\text{C min}^{-1}$ from room temperature to between 400 and 650°C , with the heat flow measured versus temperature. The samples were analyzed in both air and nitrogen, at a flow rate of $25\text{ cm}^3\text{ min}^{-1}$.

2.4. Proton conductivity measurements

Proton conductivity tests were carried out on chitosan membranes that were synthesized in the authors' laboratory. To verify the experimental procedures and interpretation of data, tests were also done on Nafion 117 membranes supplied by Ion Power, USA. Measurements were carried out in both two- and four-point-probe conductivity cells that were designed and constructed in-house.

The four-point-probe conductivity cell frame was made of two Teflon blocks, with an open 'window-like structure' employed to allow determinations of the conductivity of fully- and partially-hydrated membranes. Two, stainless-steel, wire electrodes were used to apply current to the ends of the membrane sample, while another pair of electrodes (2.25 cm apart) was used to measure the voltage drop along the film near the centre of the sample. The membrane samples were sandwiched between the two blocks that were pressed together by four screws fastened with approximately the same torque to ensure good electrode–membrane contact (Fig. 2).

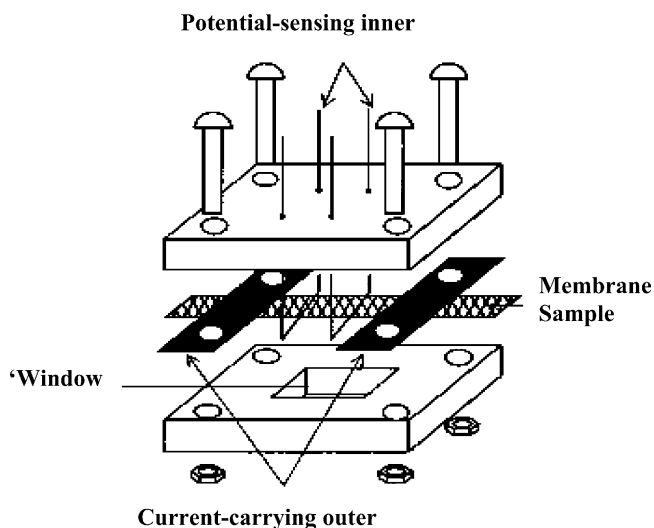


Fig. 2. Schematic view of proton conductivity cell for four-point-probe electrochemical impedance spectroscopy technique. In a four-point proton conductivity cell, a fixed ac current is passed between two outer electrodes, and the conductance of the material of interest is calculated from the ac potential difference observed between two inner electrodes. In this way, contact resistance, lead resistance, and lead inductance are almost completely eliminated.

The two-point-probe conductivity cell frame was also machined from Teflon material and two stainless-steel electrodes were used to contact the membrane on both sides. In order to reduce capacitance effects, electrodes of 1.5 mm diameter were used. Good membrane–electrode contact was ensured by way of a spring that was linked to one of the electrodes. Impedance measurements were carried out over the frequency range 1 MHz to 1 Hz at open circuit potential with an ac voltage of 5 mV, by means of a frequency response analyzer (Solartron Schlumberger 1255 HF Frequency Response Analyzer) and a potentiostat (EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A with Electrometer interface Model 273 A). Fitting of impedance data was performed with commercial software (EQUIVCRT.PAS) written by B.A Boukamp, University of Twente, The Netherlands. H_2O_2 and H_2SO_4 , both chemicals of analytical grade supplied by Sigma–Aldrich, were used in the pretreatment of the membrane samples.

2.4.1. Nafion 117 membrane

The membranes were pretreated according to the procedure adopted by Zawodzinski et al. [5]. First, they were boiled in a 3% H_2O_2 aqueous solution for 1 h, then rinsed in boiling de-ionized water repeatedly, boiled in 0.5 M H_2SO_4 for 1 h, and finally rinsed again in de-ionized water. The pretreatment of the membranes in H_2O_2 served to oxidize any small contaminants that might block the ion-conduction channels. The H_2SO_4 reverted all acidic sites to the proton form, and the de-ionized water rinsed away the excess acid. This pretreatment removed the discoloration that was typically present in the as-received membranes. The membranes

were stored in de-ionized water after pretreatment in order to ensure equilibration prior to use in conductivity measurements.

In the four-point-probe conductivity cell, conductivity was determined for partially-hydrated (25 °C) and fully-hydrated membranes (50 and 60 °C). For full hydration, the cell was fully immersed in de-ionized water. Before assembly of the cell, membrane samples were cut into strips ‘approximately 3.3 cm wide, 4 cm long and 0.02 cm thick’ that were surface dried with tissue paper and inserted between the two Teflon blocks.

Before testing in the two-point-probe conductivity cell, the membrane samples were equilibrated with 0.1 M H_2SO_4 for 24 h. The cell reservoir was filled with the same solution and the membrane was placed between the two electrodes in the solution. Impedance spectra were obtained in four different locations on the membranes to average out local variations in thickness and material properties.

2.4.2. Chitosan membranes

The chitosan membranes used in this study were not subjected to the pretreatment described above for Nafion membranes. This is basically because during synthesis, the membranes were cross-linked and protonated at the same time, in sulfuric acid. Nevertheless, two different concentrations of sulfuric acid were used (0.5 and 1 M) to see what effect the different concentrations might have on proton conductivity. After synthesis, the membrane samples were stored in de-ionized water. Sample strips of 3.3 cm wide and 4 cm long but various thicknesses (due to manual casting of membrane) were cut and surface dried before assembly of the cell. Proton conductivity measurements of chitosan membranes were performed by means of the four-point-probe technique for fully- and partially-hydrated membrane samples as it was found that results obtained using this technique for Nafion 117 membrane (standard membrane) were reliable and reproducible.

3. Results and discussion

3.1. Water uptake

The initial wet weights of representative samples of Nafion 117 and chitosan membranes before drying are shown in Table 1. Samples S1, S2, S3 and S4 correspond to those dried using procedures 1, 2, 3 and 4, respectively. The data also include the weight loss (%) of the membrane samples after drying.

After rehydration at the three water temperatures (27, 65 and 100 °C) the membrane samples gained weight and Table 2 shows the weight gains (mass %) in relation to the dry weights after rehydration.

The water uptake of chitosan membranes rehydrated at 27 °C do not show such a strong dependence on the drying temperature, as is the case with Nafion membranes. Chi-

Table 1
Wet and dry weights of membrane samples

Membrane sample	Initial wet weight (g)	Dry weight (g)	Weight loss (%)
Nafion 117 (S1)	0.0935	0.0715	30.7
Nafion 117 (S2)	0.0936	0.0703	33.1
Nafion 117 (S3)	0.0937	0.0701	33.7
Nafion 117 (S4)	0.0935	0.0693	34.9
Chitosan (S1)	0.0365	0.0154	57.8
Chitosan (S2)	0.0314	0.0122	61.2
Chitosan (S3)	0.0293	0.0122	58.4
Chitosan (S4)	0.0315	0.0120	61.9

Table 2
Mass (%) water uptake of membrane samples after rehydration in liquid water at different temperatures

Membrane sample	27 °C (%)	65 °C (%)	100 °C (%)
Nafion 117 (S1)	30.5	30.8	30.8
Nafion 117 (S2)	18.5	23.2	25.7
Nafion 117 (S3)	33.0	33.2	33.5
Nafion 117 (S4)	20.1	21.4	26.1
Chitosan (S1)	56.9	65.9	– ^a
Chitosan (S2)	52.7	66.2	– ^a
Chitosan (S3)	54.3	71.6	– ^a
Chitosan (S4)	53.1	66.3	– ^a

^a Chitosan membranes disintegrated in boiling water.

tosan membrane S1 (dried at room temp) and S3 (dried over P₂O₅) absorbed between 93 and 98% of the water that they lost upon drying. While S2 and S4 absorbed about 86% of their lost water. In other words, it can be said that chitosan membranes dried at elevated temperature and rehydrated at 27 °C exhibit less rehydration capacity than those that were not. Upon rehydration of chitosan membranes at 65 °C, it is

observed that all the four membrane samples became soft and deformed and that their respective weights are slightly more than the original weights. The membranes that were rehydrated in boiling water (100 °C) disintegrated completely on immersion in boiling water and as such, no rehydration results were recorded. No other published reports on chitosan membrane water uptake studies have been found.

3.2. Thermal stability

The weight loss (%) (TG), the derivative of weight loss (DTG) and DSC against temperature for Nafion 117 in the presence of oxygen (in air) are given in Fig. 3. These studies were conducted to relate the thermal events detected in the TG to those detected in the DSC so as to obtain a better understanding of the thermal decomposition of Nafion 117 membrane. The TG, DTG and DSC results for Nafion 117 membrane in the absence of oxygen (in nitrogen) are presented in Fig. 4. The TG/DTG/DSC results for chitosan membranes analyzed in both air and nitrogen are shown in Figs. 5 and 6.

Cross-linked chitosan membrane samples analyzed in air (Fig. 5) show a four-stage decomposition process. The first stage takes place between 30 and 200 °C with an almost 10% loss of the initial weight. This is followed by a further 40% weight loss just above 200 °C and ends at around 250 °C. The third stage of decomposition that ends at around 400 °C indicates a weight loss of about 15%. A complete weight loss is attained in the final stage of the sample decomposition starting at around 400 °C and ending just above 500 °C. TG analysis in nitrogen shows a three-stage decomposition procedure with the initial 10% weight loss taking place between 30 and 200 °C. The highest weight loss of

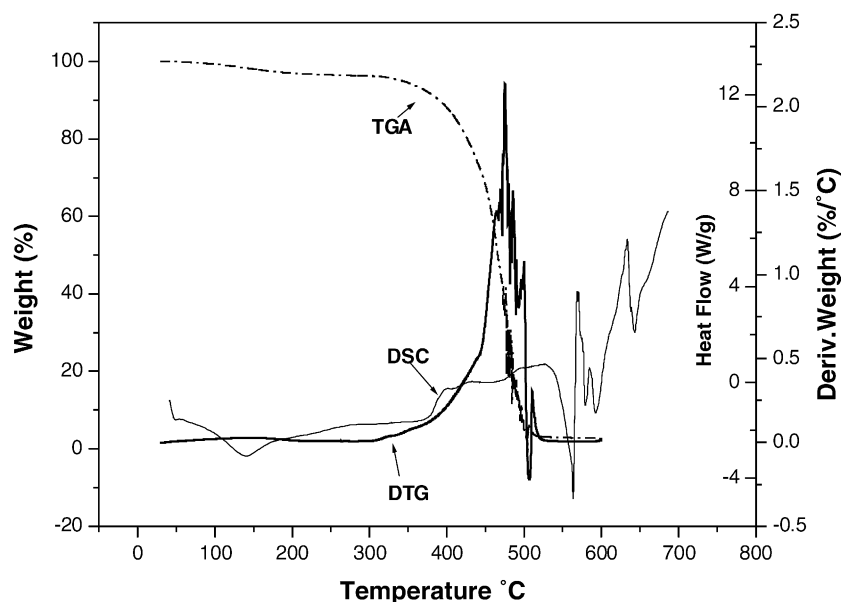


Fig. 3. TG/DTG/DSC curves for Nafion 117 in air. Weight loss (TG), derivative of weight loss (DTG) and DSC curves are overlaid so as to obtain a better understanding of the thermal decomposition mechanism of Nafion 117 in the presence of oxygen (in air).

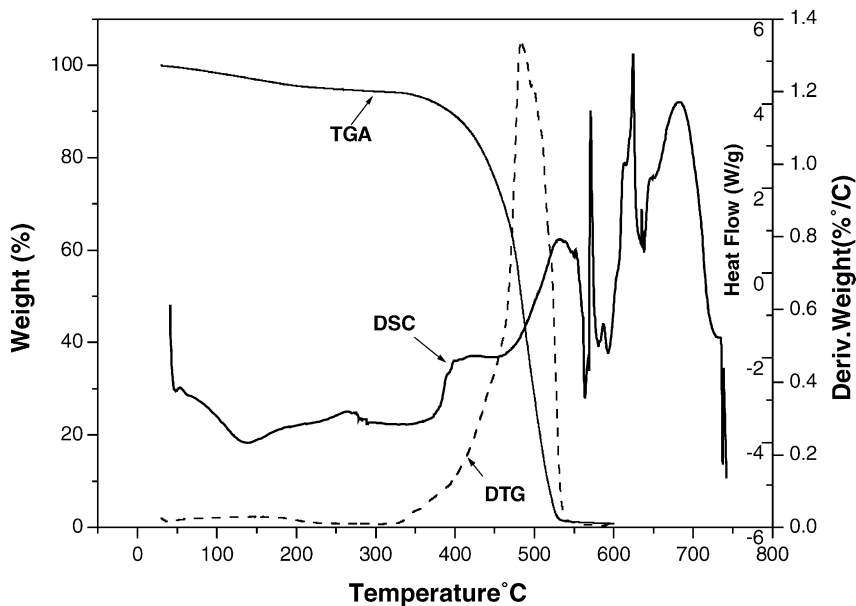


Fig. 4. TG/DTG/DSC curves for Nafion 117 in nitrogen. Weight loss (TG), derivative of weight loss (DTG) and DSC curves are overlaid so as to obtain a better understanding of the thermal decomposition mechanism of Nafion 117 in the absence of oxygen (in nitrogen).

about 40% is observed in the second stage of decomposition procedure that starts just above 200 °C and terminates at around 280 °C. A complete weight loss is not attained for MMW chitosan membrane samples in nitrogen, even after heating the material up to 650 °C, as can be seen from the third decomposition stage that starts above 280 °C.

From the results of chitosan membrane thermal analysis shown in Figs. 5 and 6, a broad endothermic peak is observed

between 40 and 150 °C. According to the work of Rueda et al. [6], this endotherm is related to the evaporation of water present in the samples that occurs over a large temperature interval. The DSC exothermic peaks at around 210 °C (Fig. 5) and 230 °C (Fig. 6) can be attributed to glass transition. The DTG curves in both graphs have transition peaks at roughly the same temperatures and these peaks are also associated with the onset of the second stage of decomposition

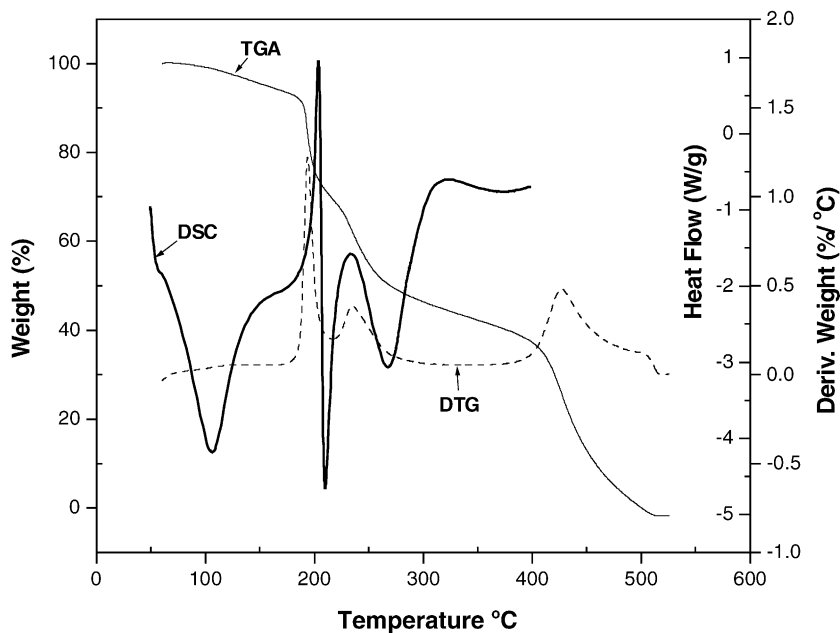


Fig. 5. TG/DTG/DSC curves of chitosan membrane in air. Weight loss (TG), derivative of weight loss (DTG) and DSC curves are overlaid so as to obtain a better understanding of the thermal decomposition mechanism of chitosan membranes in the presence of oxygen (in air).

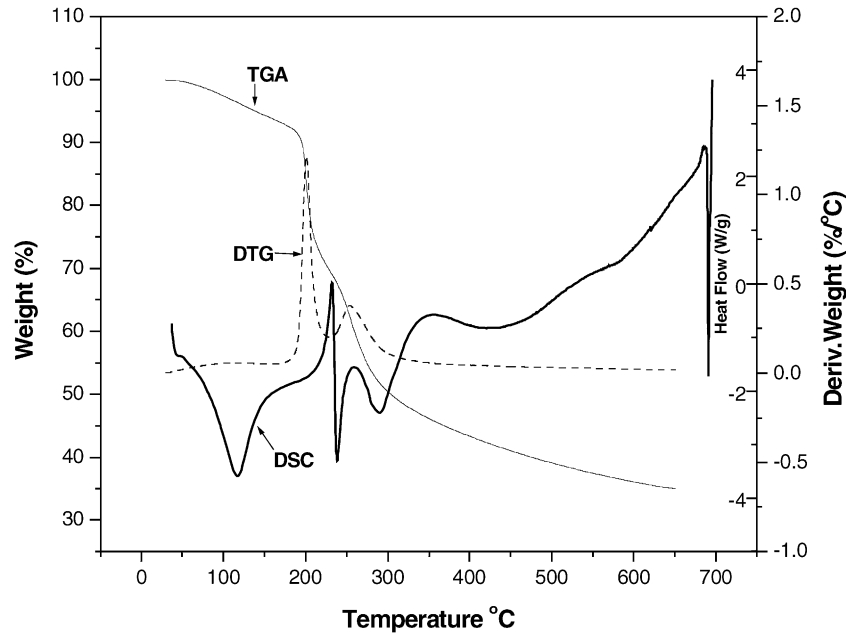


Fig. 6. TG/DTG/DSC curves of chitosan membrane in nitrogen. Weight loss (TG), derivative of weight loss (DTG) and DSC curves are overlaid so as to obtain a better understanding of the thermal decomposition mechanism of chitosan membranes in the absence of oxygen (in nitrogen).

in both air and nitrogen environments. The glass transition temperature for chitosan was reported to be 203 °C by Sakurai et al. [7]. A search for literature on the thermal stability of chitosan membranes cross-linked with sulfuric acid has yielded very little, which makes it difficult to ascertain the decomposition mechanism. From the TG/DTG/DSC curves, however, it can be seen that whatever thermal activities were induced by weight losses in the TGA were reproduced in the DSC either as exotherms or endotherms and this gives some degree of credibility to the employed techniques.

3.3. Proton conductivity

Using the membrane resistance values determined from the Nyquist plots and the cell constants, the proton conductivity was calculated using the formula for a uniform current distribution:

$$\sigma (\text{S cm}^{-1}) = \frac{L}{R \times A} \quad (2)$$

where σ is the proton conductivity (S cm^{-1}); L the distance between the two inner (potential sensing) electrodes (cm); R the determined resistance of the membrane sample from the Nyquist plot (Ω); A the cross-sectional area of the membrane (cm^2).

At all levels of hydration and temperature, Nafion 117 membranes display superior proton conductivity (an order of magnitude higher) compared with chitosan membranes. Partially-hydrated chitosan membranes at 25 °C have a proton conductivity of $(4.6\text{--}5.5) \times 10^{-3} \text{ S cm}^{-1}$ compared with $(7.7\text{--}8.2) \times 10^{-2} \text{ S cm}^{-1}$ for Nafion 117 under the same conditions. The same trend is seen at full hydration and higher temperatures with a Nafion conductivity of about $8.7 \times$

Table 3

Calculated proton conductivities of Nafion 117 and MMW chitosan membranes

Membrane type	Temperature (°C)	Proton conductivity, σ (S cm^{-1})
Nafion 117	25 (partially hydrated)	$(7.2 \pm 0.5) \times 10^{-2}$
MMW chitosan	25 (partially hydrated)	$(5.0 \pm 0.5) \times 10^{-2}$
Nafion 117	25 (fully hydrated)	9.0×10^{-2}
MMW chitosan	25 (fully hydrated)	$(9.6 \pm 0.4) \times 10^{-2}$
Nafion 117	60 (fully hydrated)	$(12.9 \pm 0.2) \times 10^{-2}$
MMW chitosan	60 (fully hydrated)	2.3×10^{-2}

$10^{-2} \text{ S cm}^{-1}$ versus $(8.7\text{--}11.8) \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C for chitosan membranes. At 60 °C (full hydration) the, proton conductivity of Nafion membranes ($\sim 13 \times 10^{-2} \text{ S cm}^{-1}$) is about six times higher than that of chitosan membranes ($(2\text{--}2.3) \times 10^{-2} \text{ S cm}^{-1}$) (Table 3).

The above results have also shown a dependence of proton conductivity of both Nafion 117 and cross-linked MMW chitosan membranes on the degree of hydration and temperature. Fully-hydrated Nafion 117 and chitosan membranes exhibit higher conductivity than partially-hydrated membranes. The results from the fully-hydrated membranes at 60 °C indicate that although water is an important factor in proton conductivity, temperature also plays an important role in overcoming activation barriers for proton motion [8].

4. Conclusions

Although chitosan membranes take up more water than Nafion at room temperature, their use in fuel cells at higher

temperatures is not possible because of their instability at higher temperatures. Only fuel-cell operations at low temperatures can be sustained.

From the decomposition curves of Nafion 117 and chitosan membranes and without the analysis of the decomposition products, it can be concluded that the Nafion 117 membrane is more thermally stable than the investigated MMW chitosan membrane, i.e., Nafion starts decomposing between 270 and 300 °C while chitosan begins to decompose at around 200 °C. The use of a chitosan membrane at higher temperature becomes difficult because its stability cannot be ensured.

At all the levels of hydration and temperature investigated, Nafion 117 membranes provide superior proton conductivity to that of chitosan membranes. Proton conductivity in both membrane materials increases strongly with increase in temperature and degree of hydration. The highest conductivity is found at 60 °C (highest temperature tested) under full hydration.

A successful fuel-cell membrane must be an effective proton conductor, be stable at higher temperatures, and also exhibit high water uptake and retention capabilities. From the results obtained here, chitosan membranes have better water uptake properties, but poorer thermal stability and proton conductivity properties than Nafion 117. High proton conductivity most often implies an ionic and strongly hydrophobic environment, like that provided by the fixed charges bound in Nafion. In hydrophilic polymers, such as chitosan, the low dielectric constants may encourage ion-pair formation, that, thereby, results in very low proton conductivity. As material for pervaporation membranes, chitosan membranes are more permeable to water than methanol. The protons are not, however, transported by a mechanism similar to water and this has an adverse effect on proton conductivity [9].

It should be noted that all the measurements described in this work were obtained with stand-alone membranes. Under conditions of fuel-cell operation, relative humidity and temperature are significantly different. It should also be pointed out that the membranes studied in this work were allowed to swell to their equilibrium values. In fuel cells, membranes operate under significant mechanical pressure

that acts in opposition to osmotic pressure. Nevertheless, any membrane synthesis and characterization study enables the development of detailed predictive models, and definition of the membrane characteristics that require improvement in order to achieve increased performance and reliability. Therefore, these results should serve to help in understanding the various properties of proton exchange membranes that are necessary for fuel-cell applications and also assist in the design of membranes with better properties.

5. Recommendations

Chitosan provides a low-cost source of membrane material and, in future work, a way of increasing its thermal stability and ionic conductivity should be investigated. The testing of synthesized chitosan membranes in a fuel-cell set up should also be considered.

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