

Effect of Relative Humidity and Temperature on the Mechanical Properties of PFSA Nafion™-cation-exchanged membranes for Electrochemical Applications

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Received: 3 November 2016 / Accepted: 19 January 2017 / Published: 12 February 2017

Perfluorosulfonic acid (PFSA) polymer membranes, also known as PEM (proton-exchange membranes), such as Nafion™ are widely used as electrolyte thin films in electrochemical hydrogen energy systems such as fuel cells, electrolyzers and electrochemical hydrogen compressors. In the present work the effect of temperature and relative humidity on the elastic moduli of various PEMs were investigated through uniaxial and biaxial tensile testing. Results of the two techniques were analysed and compared to one another to determine the validity of bulge testing in the investigation of the mechanical properties of PEMs. The bulge test technique was applied to assess the effect of elevated temperatures, humidity levels and cation contamination on the rupture pressure of the membranes. The effects of cation exchange and water absorption on the mechanical strength of PEMs are discussed in terms of cation water interactions within the molecular structure of PFSA polymers.

Keywords: Nafion™, proton-exchange membrane, PFSA, membrane rupture test, biaxial strength, elastic modulus, cation contamination, relative humidity and temperature.

1. INTRODUCTION

As fossil fuel deposits continue to deplete, research and utilisation of alternative energy carriers; wind, nuclear, hydrogen *etc.* becomes increasingly necessary. Interest in hydrogen as a fuel source has grown strongly since 1990, mainly due to the advantages as an energy carrier [1]. Although hydrogen has a high energy density by weight it has a low specific volumetric energy density, and to improve the volumetric energy density of hydrogen, it is typically stored under pressure. As the

amount of hydrogen needed is high, it is essential to have an efficient hydrogen compressor capable of operating at the high pressures required (350 – 700 bar) to lower the volumetric energy density sufficiently, as it keeps the energy efficiency of the system high [2]. Electrochemical compression has shown great promise recently and seems to be the way forward as the process is fundamentally isothermal, has no moving parts, operates silently, delivers high compression efficiencies and can separate impurities from the feed hydrogen gas [3].

Perfluorosulfonic acid (PFSA) membranes are commonly used in a variety of specialised applications including: electrochemical compression, fuel cells and water electrolysis. Nafion[™] membranes are the most favoured due to its high proton conductivity, providing high charge density, low electronic resistance, good mechanical properties, relatively low gas permeability and excellent chemical stability [4-6]. Although the use of these membranes is widespread, significant gaps remain in understanding the mechanical behaviour of these materials [4-10]. More specifically, while the structure and transport properties of bulk PEMs have been extensively studied, mechanical properties of these membranes in the presence of cations are not studied in detail. Over its service life, the PFSA membranes typically undergo hundreds of cycles between wet and dry conditions, which leads to swelling and shrinking of the membranes which can result in the mechanical failure of the membranes. In the presence of ion-exchanged cations the mechanical properties might change, a topic that has not yet received attention.

Durability and cost are the main cause limiting deployment of PEM technologies at a large scale [7]. A fundamental understanding of degradation and mechanical failure of ionomer membranes is therefore required to help diminish membrane failure, which is one of the foremost fuel cell and water electrolysis stack life-limiting factors [4]. Although the chemical and electrochemical degradation of perfluorinated membranes have been investigated and reported extensively, little work has been published on mechanical degradation of the membrane [4,11]. Several researchers have pointed out that there is a lack of comprehensive information about the viscoelastic properties of membranes; particularly at elevated temperatures and humidity [12].

Accordingly, in this research the effect of elevated temperatures and relative humidity's on the mechanical properties of Nafion[™] membranes is studied. In this work, three membranes (NR-115, NR-117 and NR-1110) varying in thickness and having the same equivalent weight (EW = 1100) were investigated through uniaxial and biaxial tensile testing.. The effect of cation contamination on the mechanical properties of these materials is also studied.

2. EXPERIMENTAL

2.1. Materials

Nafion[™] NR-115, NR-117 and NR-1110 membranes (supplied by Ion Power) with nominal dry thickness of 0.13, 0.18 and 0.24 mm respectively, were used as widely studied class of PEM materials. Abbreviation used for membranes (11) refers to the EW of the membranes (EW1100) and 5, 7 and 10 refers to the thickness of membranes, respectively, measured in mil (measurement that equals one-

(Afrox) used to apply pressure is controlled by electrically actuated solenoid valves, which were simultaneously measured by a series of pressure transducers.

Cylindrical NafionTM specimens (56 mm diameter) were used and clamped inside the high-pressure cell. The high pressure cell, containing the sample, was allowed 30 min to reach equilibrium before pressure is applied to the system. Specimens were observed to form a clear deflection as the solenoid valves are opened. A strain rate of 5 mm.min⁻¹ was observed which was in accordance with the strain rate during uniaxial tensile testing. The environmental chamber (ESPEC SH-221) allowed experiments to be conducted at different combinations of environmental conditions. During the experiments, a digital camera was used to record the deflection process, after which the bulge height was determined analytically from the video footage.

To determine the elastic moduli of the membrane specimens from the membrane rupture data Equation 1 as proposed by Schomburg [14] was used. The Poisson's ratio was assumed to be 0.4 for all membranes, which was validated throughout literature for NafionTM materials [8,12-15].

$$\Delta P = \frac{4d_m w_0}{R_M^2} \left(\frac{64 w_0^2 E_M}{105 R_M^2 (1 - \nu_M^2)} \right) = \frac{4d_M w_0}{R_M^2} \sigma_R \quad (1)$$

2.3. Uniaxial tensile testing

The elastic moduli of the membranes were also determined using uniaxial tensile tests which were conducted with a mechanical test system (MTS Criterion C45.503 Universal Tensile Tester) in conjunction with an environmental chamber (ESPEC SH-221). Membranes were measured at combinations of four different relative humidity (RH) levels (35%, 50%, 70% and 90%) at 20°C. At every combination the specimen (20 mm × 120 mm) was first treated in the relevant environment for 30 min and then loaded into the mechanical test system. A constant crosshead speed of 5mm.min⁻¹ was then applied. The elastic moduli were determined from the initial slope of the stress-strain curves.

3. RESULTS AND DISCUSSION

3.1. Methodology validation

Tensile properties were determined for all the as-received membranes through uniaxial tensile testing to obtain a baseline for the comparison of results obtained from biaxial testing. It is observed from Figure. 3 that the elastic modulus (determined from biaxial testing data) is relatable with the results obtained by uniaxial testing. Further, it can be seen that the values obtained by biaxial tensile testing do not differ significantly from the values obtained by uniaxial tensile testing. On average, the values from the biaxial tensile testing method are 1.3 % lower than that obtained by the conventional method, which serves as validation that the method used for the biaxial tensile testing can be used with confidence as it is accurate and comparable to conventional uniaxial tensile testing.

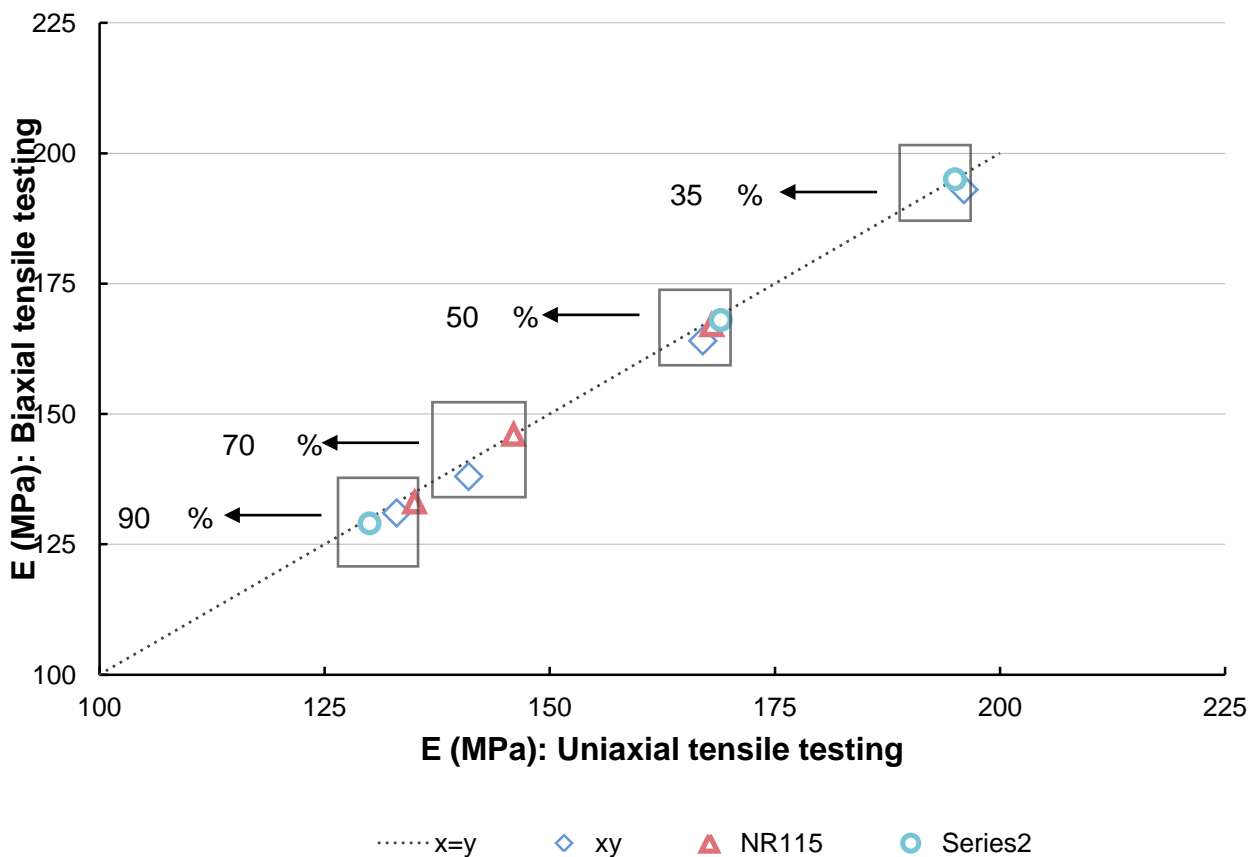


Figure 3. Comparison of Young's modulus of Nafion™ membranes (NR-115, NR-115, NR-1110) at 20 °C obtained through uniaxial- and biaxial tensile testing as a function of RH%.

The validity of the model proposed by Schomburg [14] in Equation 1, was evaluated as a function of RH at 20°C. A single value for the Young's modulus was fitted to the model to construct a theoretical line of the deflection as a function of pressure. The experimental videos were analysed after the biaxial tensile testing, and deflection and corresponding pressures were plotted against the model for comparison. The results are presented in Figure.4.

From Figure 4 it is observed that for each condition, where one fixed value is used for E with Equation 1 the model proposed by Schomburg [14] describes the deflection as a function of applied pressure accurately. The Young's modulus can thus be determined with sufficient accuracy at any point during biaxial tensile test with the measurement of the deflection and the subsequent pressure.

The model was further used to investigate the effect of the sample radius on the Young's modulus. The radius of the blister area was varied to 5, 7.5 and 10 mm, and the biaxial tensile testing was conducted at 50 % RH and 50 °C. A model line was constructed for a Young's modulus value of 106 MPa for each of the different radii. The deflection and corresponding pressure at selected points were recorded and plotted against the theoretical values to further evaluate the accuracy of the model. The results are presented in Figure 5.

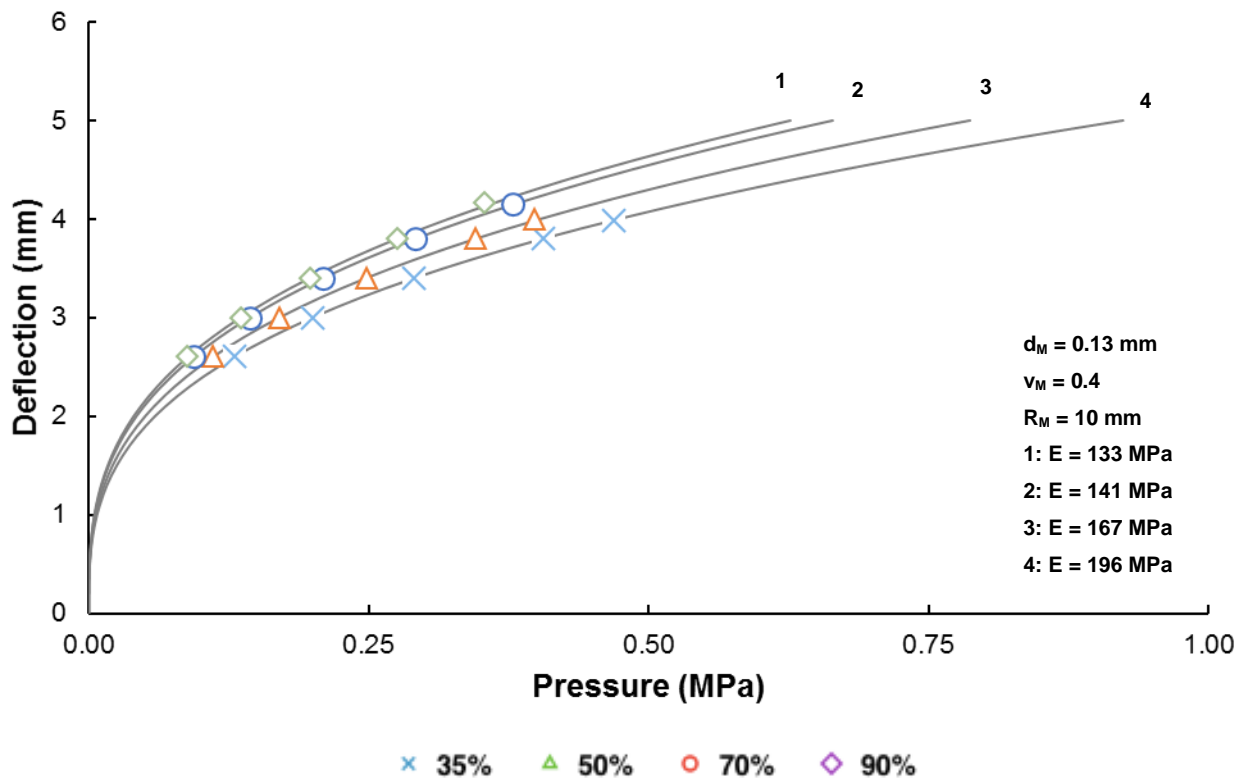


Figure 4. Deflection as a function of applied pressure and relative humidity for NR-115 and comparison with the model by Schomburg [14].

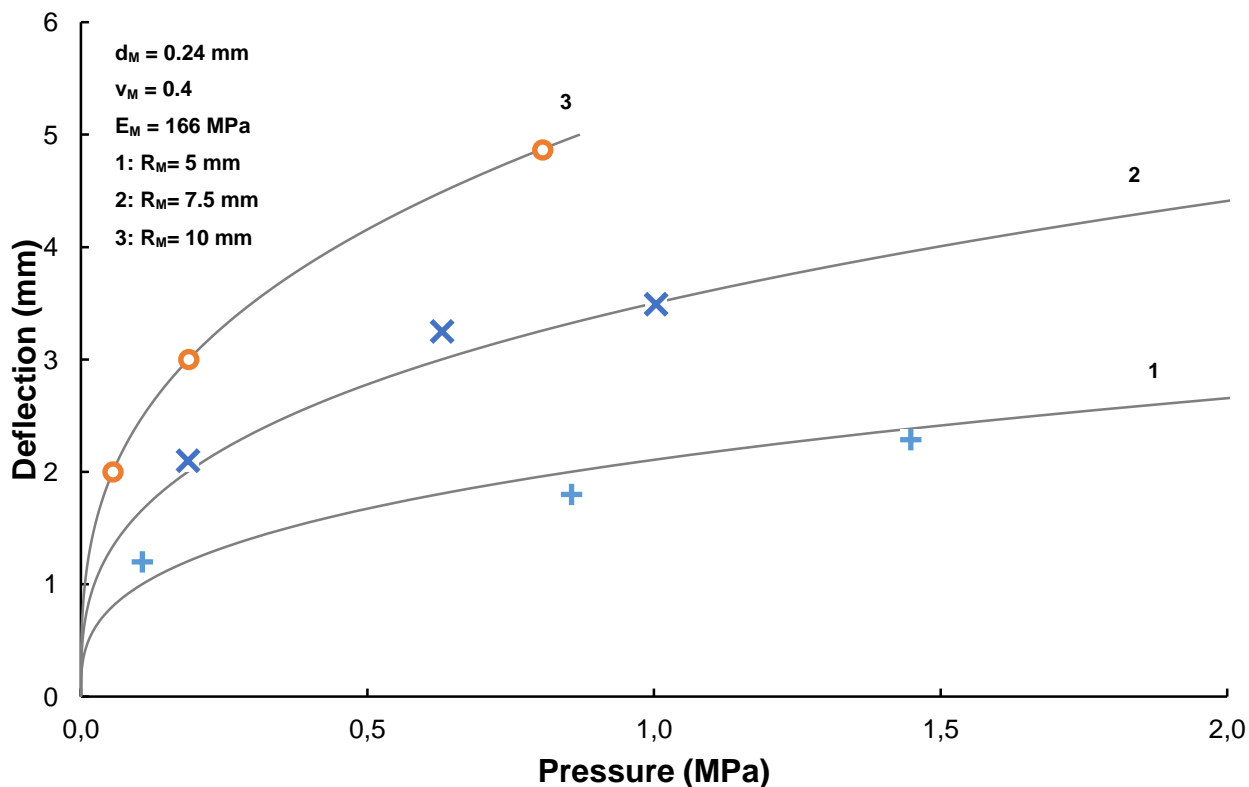


Figure 5. Deflection as a function of applied pressure and blister diameter for NR-115 at 50% RH and 50°C.

From Figure 5 it is observed that the data points recorded for each radius correlates well to the model. Slight deviations from the theoretical values are observed for sample diameters of 5 mm and 7.5 mm. A root mean square deviation of 0.1 mm have been determined for the measured values compared to the model. This equates to a maximum deviation from the model of $\pm 7\%$. The model remains valid regardless of the radius of the membrane sample. Furthermore, it can be seen that the rupture pressure (end of line) increases as the radius of the test sample decreases, whereas an increase in the deflection results from an increase of the test sample radius. A sample radius of 10 mm was selected for further experimentation as it showed the best correlation.

From these results it can be concluded that the experimental setup proposed for biaxial tensile testing is a valid alternative to conventional uniaxial tensile testing, and that the model of Schomburg [14] can be used to related deflection with pressure. One advantage off this model is also that the atmospheric conditions (specifically) relative humidity can be better controlled compared to conventional uniaxial testing units.

3.2. Bulge testing on as received PEMs

Biaxial testing was then used to determine the elastic modulus of the NR-1110 Nafion™ membranes at a combination of three temperatures and four RH levels.

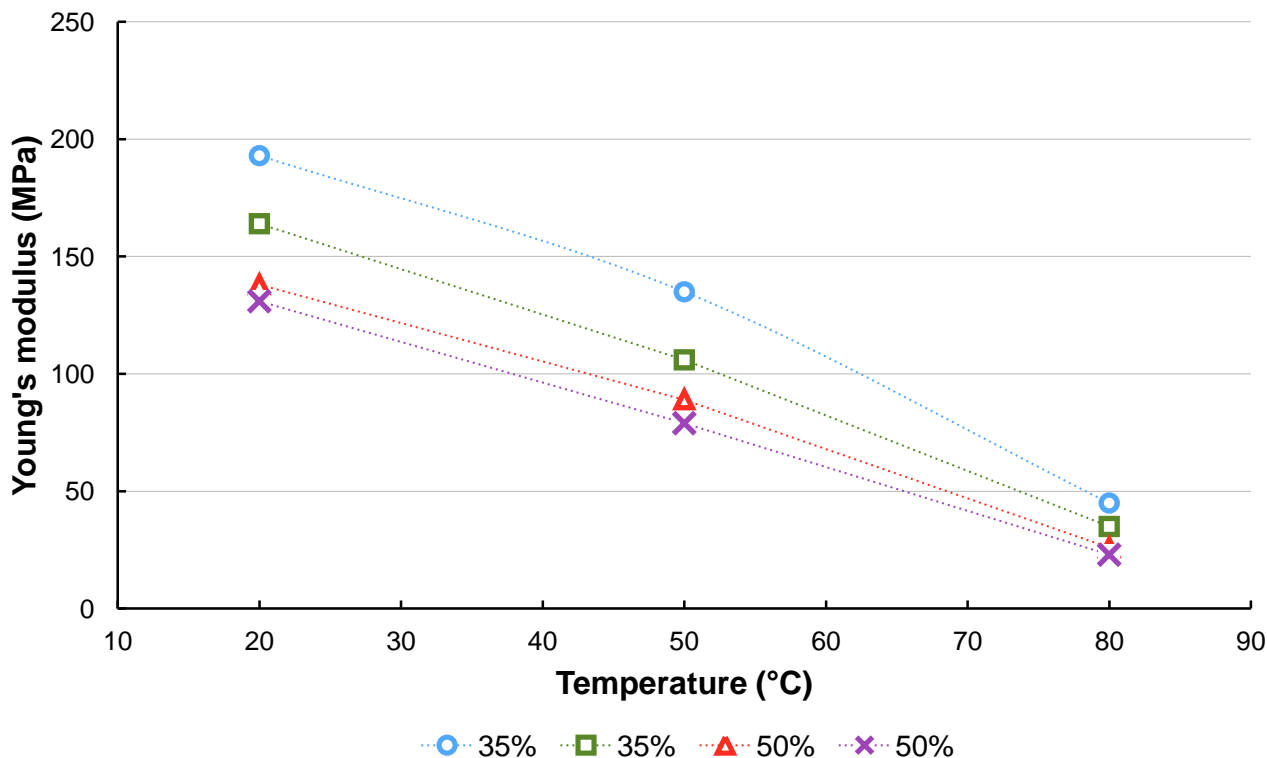


Figure 6. Average Young's modulus of NR-1110 Nafion™ membranes determined through biaxial tensile testing as a function of RH and temperature.

In Figure 6 it is observed that the elastic modulus decreases with an increase of RH and temperature, with the temperature variation having the greater influence of the two parameters. The decrease of the elastic modulus with increasing RH can be contributed to the plasticisation of the PFSA polymer upon water absorption, especially at higher temperatures [13]. As water diffuses into the membrane, the isolated clusters formed by sulfonic acid groups swells and forms spherical water pools. This leads to a reduction of intermolecular forces and ionic interaction between sulfonate groups, which weakens the strength of the membranes [16]. An increase in temperature tends to weaken the cross-linking of polymeric chains by destroying cluster structures. This results in a decrease in stiffness of the membranes and thereby a reduction of the elastic modulus [13,17]. The results are also in line with reported in literature as summarised in [20].

3.3. Bulge testing on PEMs after ion exchange process

In Figure 7 it is illustrated that the Young's modulus of the samples increases in the order H^+ , Na^+ , Mg^{2+} , Fe^{3+} . The increase in the Young's modulus can be attributed to several factors, which are based on the premise that the mechanical and viscoelastic properties of NafionTM are mainly dependent on the water content in the membrane.

The reference membrane for the contamination tests contains only the H^+ cation thus all sulfonic acid groups are occupied by H^+ ions within the matrix of the membrane. This physical structure allows for maximum uptake of water due to the formation of hydronium ions, weakening the membrane.

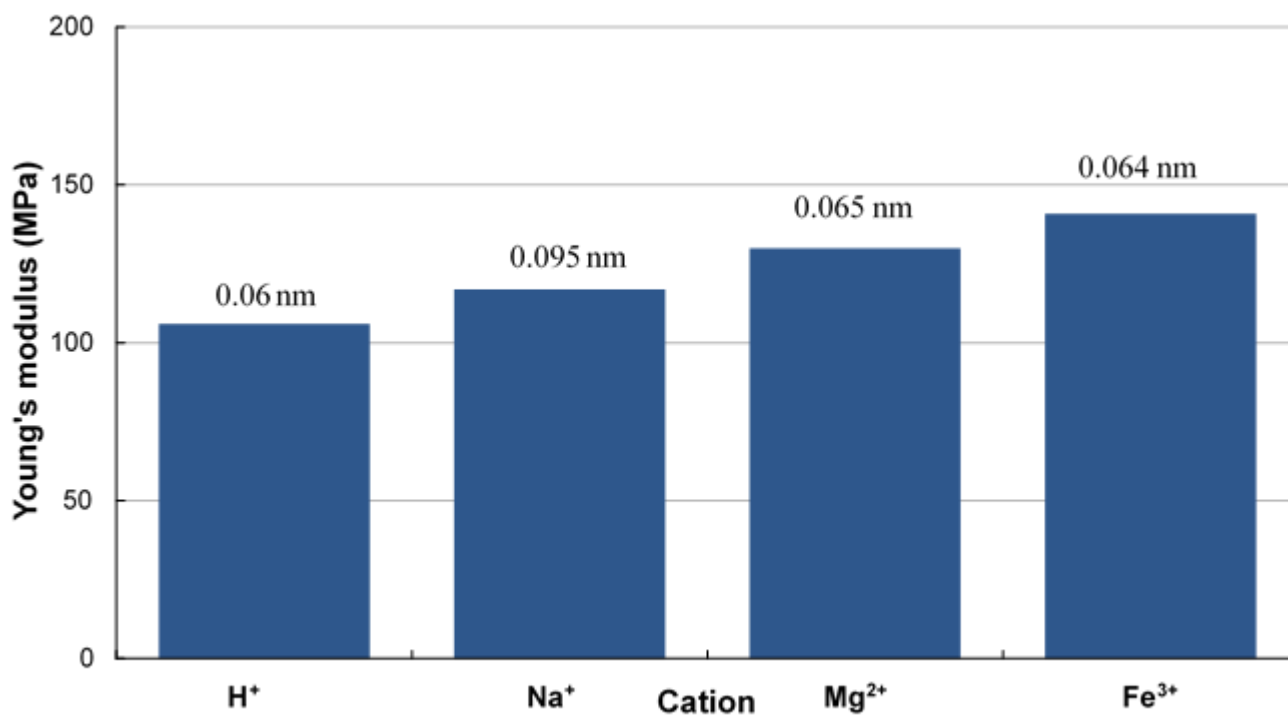


Figure 7. Young modulus of cation-contaminated non-reinforced NafionTM NR-1110 (240 μ m) membranes at 50°C and 50% RH. The inserted numbers are the cation radius for the specific species [19].

As a result of cation exchange, the sulfonic acid groups are occupied by cations, replacing the H^+ , which affects the water uptake of the material. The presence of the other cations causes the mobility of the sulfonic acid groups to decrease, lowering the flexibility of the side chains around the cluster which results in the structural stiffness and consequently the Young's modulus of the membrane to increase [18]. When multivalent cations such as magnesium (2+) and iron (3+) are used in the contamination process, it is believed that two or even three acid sites are attached to the metal ion [13,19]. This effect reduces the overall water uptake of the membrane, and hence an increase in strength could be expected. There is thus a correlation between the Young's modulus, ion valence and charge density. Similar results have been reported by Collier *et al.* [17], Jai *et al.* [13] and Kundu *et al.* [18].

4. CONCLUSION

In this study, the effect of temperature, relative humidity and cation contamination on mechanical properties of 1100 EW Nafion™ proton exchange membranes with various thin film characterisation techniques was studied. The uniaxial tensile testing implemented was used to obtain an accurate baseline for data through bulge testing. Bulge tests were applied to assess the biaxial mechanical behaviour of the PEMs using high pressure nitrogen gas as pressurisation medium in conjunction with an environmental chamber to simulate various operating conditions for electrochemical hydrogen devices. The elastic moduli of Nafion™, determined through uniaxial and biaxial testing, showed to be reliable under selected temperature and RH conditions. It was found that the elastic moduli decreased with increase of temperature and RH. The Young's modulus increased with increasing valence of the cations exchanged. These behaviours were explained in terms of cation - and water interactions within the molecular structure of PFSA polymer membranes.

Nomenclature

ΔP	Pressure differential (MPa)
d_m	Membrane thickness (mm)
w_0	Deflection (mm)
R_M	Radius (mm)
E_M	Elastic modulus (MPa)
ν_M	Poisson's ratio
σ_R	Radial stress (MPa)

ACKNOWLEDGEMENTS

The authors thank DST HySA Infrastructure centre of competence for their support of this work.

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