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GO-Nafion Composite Membrane Development for Enabling Intermediate Temperature Operation of Polymer Electrolyte Fuel Cell

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Abstract

Increasing Polymer Electrolyte Fuel Cells' (PEFCs) operating temperature has benefits on the performance and the ease of utilisation of the heat generated; however, efforts for high temperature PEFCs have resulted in high degradation and reduced life time. In the literature, conventional low temperature ($T < 80^{\circ}\text{C}$) and high temperature ($140\text{-}200^{\circ}\text{C}$) regimes have been extensively studied, while the gap of operating at intermediate temperature (IT) ($100\text{-}120^{\circ}\text{C}$) has been scarcely explored.

The main bottleneck for operating at IT conditions is the development of a suitable proton exchange membrane with comparable performance and lifetime to the commercially used Nafion operating at conventional conditions. In this work, composite membranes of Graphene Oxide (GO) and Nafion of varied thickness were fabricated, characterised and assessed for in-situ single cell performance under automotive operating conditions at conventional and intermediate temperatures.

The material characterisation confirmed that a composite GO-Nafion structure was achieved. The composite membrane demonstrated higher mechanical strength, enhanced water uptake, and higher performance. It was demonstrated that by utilising GO-Nafion composite membranes, an up to 20% increase in the maximum power density at all operating temperatures can be achieved, with the optimum performance is obtained at 100°C . Moreover, the GO-Nafion membrane was able to maintain its open circuit voltage values at increased temperature and reduced thickness, indicating better durability and potentially higher lifetime.

1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) are electrochemical devices that convert the chemical energy in hydrogen fuel into electrical power and heat. Due to the high efficiency, zero emissions at point of use and fast response to load change, they have been identified for replacing the internal combustion engine in vehicles. One of the main technical challenges in membrane development for the next generation of automotive PEFC stacks is to increase the operating conditions up to 105°C and to reduce the membrane thickness to increase the MEA performance while maintaining the fuel cells' lifetime. The targets were highlighted in the recent European Fuel Cell and Hydrogen Joint Undertaking call for projects (FCH-01-4-2019) [1].

The performance of a PEFC relies on achieving high proton conductivity in the polymer electrolyte which is dependent on its level of hydration [2]. The conventional perfluorosulfonic acid polymer electrolyte limits PEFC operating temperature to 80°C, due to dehydration above this value which results in loss in proton conductivity, and high degradation rates at elevated temperatures. However, operating at temperatures above 100°C provides many benefits including; improved reaction rate, simplified water management and enhanced heat rejection [3].

Therefore, High Temperature (HT) PEFCs have been developed using a phosphoric acid based membrane. HT-PEFCs operate at a temperature range of 140-200°C and can tolerate higher level of contaminants in the fuel. However, despite the extensive effort to improve the durability of the membranes, HT-PEFC suffer from high degradation rates due to phosphoric acid leaching, and of low performance in comparison to conventional PEFC. Moreover, as the minimum temperature for operation was increased to 140°C, the cells do not display the fast start-up time required for the automotive industry [4].

Recently, research has looked into ways of modifying the Nafion polymer structure to allow operating it at temperatures up to 120°C, coining the term 'Intermediate Temperature' (IT)-PEFC. The approach taken was to introduce fillers into the polymer structure to modify its properties, namely; mechanical strength, water retention at high temperatures and/ or dry conditions, or further enhance proton conductivity. The majority of the work on composite membranes has been for direct methanol fuel cells, with the aim of reducing methanol crossover through the membrane [5]–[12].

Composite membranes have been fabricated with a variety of fillers, namely organic and inorganic materials. PTFE [13]–[15] and PVA [16], [17] have been used as organic fillers with Nafion to enhance mechanical properties and provide extra durability [15], [18]. The work on organic fillers has been extensively reviewed by Branco et al. [19].

Studies on inorganic filler materials included metal oxides; such as, titanium oxide [20]–[23], zirconium oxide, and silicon oxides [24]–[29], and carbon nano-materials[30], [31]. These materials were used due to their hydrophilic properties which would assist the membrane to retain water in its structure at high temperatures or dry conditions. Moreover, cerium oxide nanoparticles [32], [33] have been used to remove peroxide radicals that are formed during fuel cell operation to improve durability and lifetime. Furthermore, the filler materials incorporated into the nafion polymer matrix can also be

functionalised providing improved, or completely new properties, for example, increased proton conductivity via sulphonation [31], [34], [35], [36]. The work on inorganic fillers has been extensively reviewed by Bakangura et al. [37].

Graphene Oxide (GO), which exists in a honeycomb lattice, is a highly hydrophilic material and exhibits a reasonable level of proton conductivity [38]. It was reported that the incorporation of GO into the Nafion electrolyte increases the mechanical strength and gas impermeability of the membrane [39] [40]. When operating at high temperatures, the hydrophilic properties of GO become notable as humidity is retained and this facilitates the proton transfer dependent on good water uptake [41]. The increased insulation properties of GO also prevent electrons from being transported along the membrane, hence improving performance and efficiency [42] [43]. The performance of Nafion recast and GO-Nafion composite membranes was compared in-situ in a single cell at temperatures above 100 °C and low relative humidity, and the results showed better performance for the composite membrane [44] [45].

The work on graphene oxide based nafion membranes has been reviewed by Pandey et al. [46]. Zarrin et al. [47] fabricated composite membranes with graphene oxide filler functionalised with sulphonic groups for the purpose of operating at an elevated fuel cell temperature. The functionalised graphene oxide resulted in an increased water uptake of 6 % for a composite membrane with 10 % loading, compared to recast nafion. In addition, the proton conductivity of the functionalised composite membrane was more than 4 times greater than Nafion at 120 °C and 30% RH; an increase from 0.012 S cm⁻¹ to 0.047 S cm⁻¹. The authors' explain that the very large surface area of graphene oxide and the large amounts of sulphonated groups allows the membrane to hold more water that can aid in the transport of protons via the Grotthuss mechanism. Single cell tests at 120 °C and 25% RH reveal that the composite membrane with 10% loading has a peak power density of 0.15 W cm⁻², which is much greater than that of recast Nafion (0.042 W cm⁻²). Bai et al. [48] prepared composite membranes consisting of chitosan polymer and phosphorylated graphene oxide and these membranes exhibited improved mechanical. The composite membranes of varying loading revealed tensile strengths between 49 and 51 MPa, much greater than the 44.7 MPa of chitosan. However, the addition of filler resulted in a decrease in elongation at break. Proton conductivity tests performed at 120 °C and 0% RH showed that the chitosan/phosphorylated graphene oxide with 1.5 % loading had a proton conductivity of 3.37 mS cm⁻¹, in comparison to 0.17 mS cm⁻¹ for the chitosan alone. In addition, activation barriers for conduction were measured and the composite membrane displayed both Grotthuss and vehicle mechanisms. Single cell testing, under the same conditions showed that the composite membrane had an OCV of 0.98 V and a max power density of 107 mW cm⁻². Vinothkannan et al. [49] produced composite membranes consisting of nafion, sulphonated graphene oxide and iron oxide nanoparticles. The composite membrane revealed higher thermal stability via greater residual mass (8.24%), compared to that of 0.26 % for pristine Nafion. The composite membrane also displayed an increased proton conductivity of almost 5 times of that of recast Nafion at 120 °C and 20% RH. Single cell tests under 120 °C and 25 % reveal that the composite membrane

has a max power density of 259 mW cm^{-2} , compared to 145 mW cm^{-2} for pristine Nafion. However, there were variations in thicknesses in the membranes produced. The authors' explain that since the amount of nafion was the same in each membrane that they could be compared.

Branco [50] and Lee et al. [51] investigated the use of GO as a filler, combined with Nafion in multi-layer membranes. Results from their investigations highlighted a positive performance of GO as a filler for composite membranes in PEFCs. GO composite membranes significantly improved the tensile strength of the membrane and showed high water uptake compared to pure Nafion. These membranes also showed higher proton conductivities when compared to Nafion membranes. However, the multi-layer membranes showed issues with mass transport, leading to a reduction in potential at high current density.

Moreover, another technical challenge for the automotive membrane development is the reduction of the membrane thickness to increase the fuel cell performance. Thinner membranes have lower overall ohmic resistance but higher hydrogen crossover and therefore lower lifetime [52] [53]. In recent work, Hiraiwa et al. [14] demonstrated an ultra- thin cross-linked (radiation grafted) PTFE membrane (testing membranes of thicknesses approx.. 13, 18, 23 and 73 μm) showing enhanced power density, however, the thinner MEAs had a reduced open circuit voltage (73 μm had the highest OCV and the 18 μm membrane had the highest maximum power) and higher oxygen crossover. From the impedance measurements, it was found that there was a decreasing linear relationship between thickness and ohmic resistance with the 13 μm membrane having the lowest resistance.

The work reported here is aimed at addressing two technical targets for membranes in automotive PEFCs, namely, the elevated temperature of operation, coupled with a reduced membrane thickness using the insights mentioned above. Therefore, Nafion and GO-Nafion composite membranes with variable thicknesses were fabricated, characterised, and tested in-situ under standard automotive operating conditions [54]. The performance of Nafion and GO-Nafion were compared at operating temperatures of 80, 100, and 120°C.

2. Methodology

2.1 Membrane fabrication

All membranes (recast and composite) were fabricated via solution casting method following the procedure reported in [50]. Nafion ionomer dispersion (D1021 10% in water, Ionpower) was mixed with ethanol and left in a vacuum desiccator over night to remove any dissolved gasses. For GO-Nafion composite membranes, GO (Nanoinnova) was measured to achieve a fraction of 4.5 wt % in the composite membrane and was dispersed in 4 ml of DI water using an ultrasonic probe (Sonics vibra cell) for 14 minutes (5 minutes at 60%, on and off for 5 seconds each followed by 4 minutes at 40%, 5 seconds on, 1 second off). The Nafion solution was then added to the GO dispersion and the combined solution was sonicated at 20% for a further 2 minutes (5 seconds on, 1 second off).

The solution (Nafion dispersion or GO-Nafion dispersion) was then poured into a borosilicate petri dish and placed into an oven for 2 hours at 100 °C followed by 1 hour at 120 °C. On completion, the

membrane was covered in DI water and gently removed. To achieve membranes of varying thicknesses, the quantity of Nafion ionomer dispersion used to fabricate the different thicknesses was optimised as shown in Table 1.

Table 1: Nafion dispersion quantities and membrane relative thickness.

Nafion membranes	
Nafion dispersion quantity (ml)	Thickness (μm)
4.9	50
3.6	40
3	30
GO-Nafion composite membranes	
4.2	50
3.2	40
2.4	30

The polymer membranes were then activated for proton conductivity by immersing them for 1 hour at each step at 80 °C in (i) DI water to clean the membrane, (ii) 3% hydrogen peroxide (Sigma-Aldrich) to remove any impurities, (iii) DI water again to remove any residual hydrogen peroxide, then in (iv) 0.5M sulphuric acid (Alfa Aesar) to functionalise the polymer side chain, and finally in (v) water to remove any excess sulphuric acid.

2.2 Membrane characterisation

The thermal stability of the membranes was tested with a TGA (Netzsch TG 209 F1) with nitrogen flow and heating to a maximum of 800 °C at a ramp of 5 °C/min. Moreover, the TGA results were also used to confirm the actual GO loading in the membrane. Membrane samples were freeze-cracked with liquid nitrogen and their cross section was studied by SEM (Hitachi TM3030Plus Tabletop Microscope at 5kV). The functional groups of the membranes were studied by FT-IR (Cary 660 FTIR Spectrometer, Agilent Technologies).

An Instron 5848 MicroTester was used to study the tensile properties with an extension rate of 2 mm/min. Prior to mechanical testing, the membrane samples were cut into dogbone samples (50% ASTM D638 TYPE V).

To measure the water uptake and the membrane swelling, the membrane samples were stored in vials with DI water overnight in an oven at 50°C temperature. The samples were then retrieved, surface water removed by filter paper and their weight and thickness immediately measured with a microbalance (Sartorius LA120S Lab Analytical) and a micrometer respectively. The samples were then placed in an oven for 24 hours to dry, after which their dry weight and thickness were measured. Water uptake and swelling were calculated via:

$$\text{Water uptake (\%)} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100$$

For the ion exchange coefficient (IEC) measurement, the membrane samples were kept in 0.1 M hydrochloric acid for 24 hours before removal and washed with DI water. This was followed by 72 hours in a saturated solution of sodium chloride. The samples were titrated with 0.01 M of sodium hydroxide with a phenolphthalein indicator. The IEC was calculated via:

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}}$$

Where V_{NaOH} is the volume of consumed sodium hydroxide and C_{NaOH} is the concentration of sodium hydroxide.

2.3 MEA fabrication and testing

For the in-situ testing, the activated membranes were cut into a 25 cm² square samples and hot pressed between two gas diffusion electrodes (Johnson Matthey GDE 0.4mg PT loading) of 4 cm² at 140 °C for two minutes to create an MEA.

The MEAs were tested using a Scribner 850e fuel cell test station. Before the MEA underwent any testing it was conditioned at 80 °C with 100% relative humidity, back pressures of 150 kPa and 130 kPa (anode and cathode, respectively), anode inlet of hydrogen and cathode inlet of air (1.3 and 1.5 stoichiometry, respectively) for six hours.

After which, polarisation curve and electrochemical impedance spectra were obtained using the automotive single cell testing standard; relative humidity of 50% and 30%, and back pressures of 150 kPa and 130 kPa at the anode and cathode, respectively [54], at operating temperatures of 80, 100, and 120°C. To assess the effect of GO and the membrane thickness on the durability of the membranes, the cell open circuit voltage was reported at the different temperatures.

The in-situ results obtained were used to compare the performance of recast Nafion and GO-Nafion membranes fabricated in-house. The performance of the GO-Nafion membrane was not compared to commercially available membranes to eliminate the significant effect of the fabrication process on the performance of the membrane.

3. Results and Discussion

3.1 Membrane Characterisation

SEM images of the 30µm recast Nafion and GO-Nafion composite membranes are presented in Figure 1. The recast Nafion membrane showed a smooth and consistent cross section. The composite membrane showed the GO sheets dispersed horizontally in the polymer layer and perpendicular to the direction of reactant supply to electrodes.

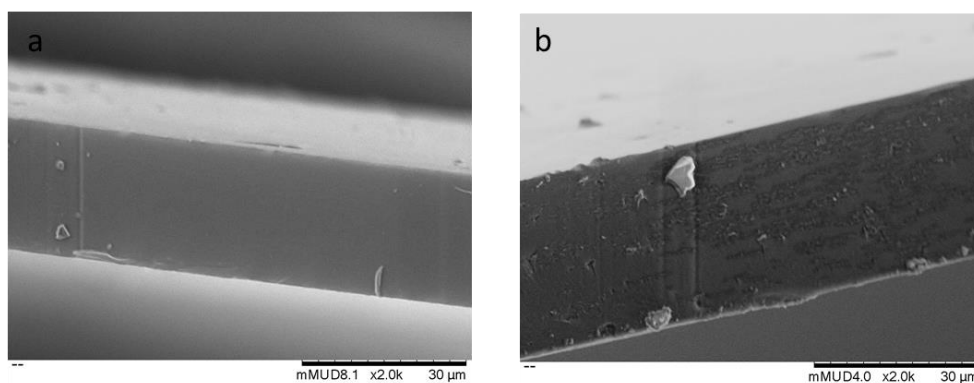


Figure 1: SEM image for a) recast Nafion, and b) GO-Nafion composite membrane.

TGA results of the Nafion and composite membrane showed similar trends with the difference in the residual weight at the end of test which was attributed to the GO loading. From around 50 to 150 °C there was a decrease in mass due to the removal of water from the membrane. Another decrease in mass was observed around 300 °C which was due to the loss of functional groups in both membranes before complete loss of the polymer chain. Whereas the Nafion weight was completely lost at temperatures over 500 °C, there was still some residue from the composite membrane. With our 4.5 wt% target loading, the TGA results revealed an actual GO loading of around 2.5 wt% which can be explained by losses in the fabrication process and the loss of GO surface functional groups.

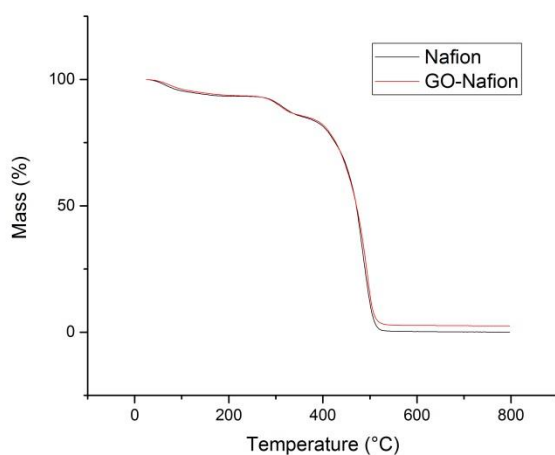


Figure 2: TGA analysis of Nafion and GO-Nafion.

Figure 3 presents the FT-IR spectrum for recast Nafion and the composite membrane. The peaks around 2900 cm^{-1} correspond to aliphatic carbon hydrogen bonds, indicating that the GO had not been completely oxidised. The double peak around 1700 cm^{-1} corresponds to various oxygen functional groups, distinguishing the composite membrane as having GO within its matrix, for example the O-H peak at 1723 cm^{-1} . This has been explained by Kumar et al. [44].

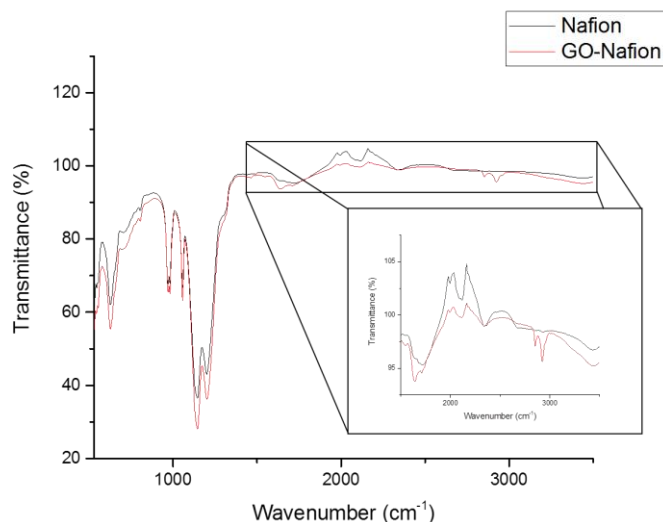


Figure 3: Fourier Transfer Infrared Spectroscopy of the recast Nafion and GO-Nafion membranes.

Figure 4 displays the stress and strain data of the recast Nafion and composite membrane. The composite membrane demonstrated higher mechanical strength and endured higher stress due to the presence of GO, which made it mechanically stronger than recast Nafion. The increased mechanical strength of the composite membrane indicates its suitability towards fuel cell application, having the potential for an extended lifetime.

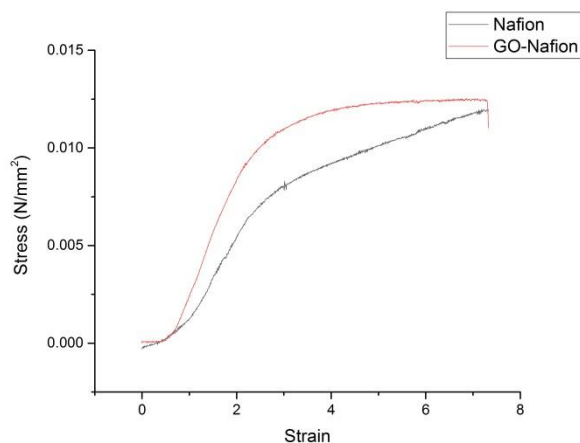


Figure 4: Recast Nafion and composite membrane stress strain curve.

Table 2 displays the membrane characteristics of water uptake, swelling, and IEC. For all thicknesses, the presence of GO in the polymer structure has led to an increase in swelling and has improved water uptake. The increased water uptake indicates an improved retention of water which leads to increased proton conductivity. However, the IEC decreases with the addition of GO. This could be because the GO has less Nafion compared to recast Nafion of the same thickness. Another reason is that the introduction of GO leads to a reduction in ionic channels [55] when compared to the

recast Nafion. However for the 30 μm membranes, the GO-nafion had a slightly lower IEC than its respective composite membrane. This result could be due to non-uniformity in the graphene oxide dispersion within the composite membrane. A non-uniform dispersion with agglomerates could potentially have a higher IEC as less ionic channels are obstructed by the graphene oxide. For the recast Nafion membrane, IEC decreases with decreasing membrane thickness as less Nafion ionomer is present in the thinner membranes, therefore reducing the transfer capacity between protons and chloride ions in the test. On the other hand, IEC change between recast Nafion and GO-Nafion membranes suggest an interaction between the polymer side chain and the GO that enables higher IEC with lower ionomer loading in the membrane.

Table 2: Water uptake, swelling, and ion exchange capacity of the fabricated membranes.

Membrane	Water Uptake (%)	Swelling (%)	IEC (meq/g)
50 μm Nafion	26.25 \pm 5.666	16.52 \pm 7.167	2.36 \pm 0.2884
40 μm Nafion	23.56 \pm 4.306	14.47 \pm 2.889	1.91 \pm 0.3962
30 μm Nafion	24.08 \pm 4.413	18.45 \pm 3.304	1.86 \pm 0.2257
50 μm GO-Nafion	29.13 \pm 4.191	21.10 \pm 5.041	1.55 \pm 0.0818
40 μm GO-Nafion	28.04 \pm 6.179	27.77 \pm 8.445	1.47 \pm 0.0760
30 μm GO-Nafion	32.86 \pm 3.62	22.53 \pm 12.073	1.89 \pm 0.1855

3.2 In-situ testing

MEAs were fabricated using the recast Nafion and GO-Nafion membranes as described above. The MEAs were tested in a single cell whilst varying the operating temperature to obtain a polarisation curve and electrochemical impedance spectra (EIS). From the polarisation curve, the maximum power density was calculated and is presented in Figure 5.a. For all the MEAs, the maximum power density was achieved at 100 $^{\circ}\text{C}$ operating temperature due to the reduction in mass transport limitation. This is also indicated by highest current densities achieved at 0.25V for all the MEAs when operated at 100 $^{\circ}\text{C}$ (Figure 5.b). Also, unsurprisingly, the reduction in the membrane thickness resulted in a general increase in the maximum power density of the MEA especially when operating at 80 $^{\circ}\text{C}$.

Only for the 50 μm membranes, the recast Nafion showed higher performance than that for the composite membranes. Both for the 30 and 40 μm thicknesses, the composite membrane had higher maximum power compared to their respective recast single layer Nafion counterparts at all temperatures. However, this was not observed for the 40 μm at 80 $^{\circ}\text{C}$, where recast nafion performed slightly better. There was also a relatively lower drop in power density when the temperature was increased beyond 100 $^{\circ}\text{C}$. This was because the graphene oxide retained more water, ensuring that

proton conductivity was less hampered as compared to the recast Nafion.

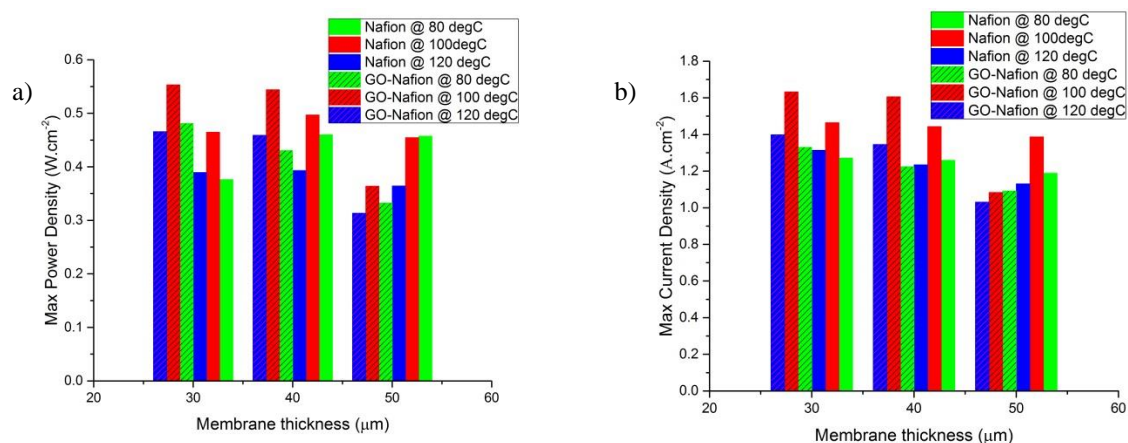


Figure 5: a) Maximum power density, and b) Maximum current density at 0.25V.

From the EIS results, the high frequency resistance of the MEAs (indicating the MEA ohmic resistance) is shown in Figure 6. As to be expected, increasing thickness resulted in higher resistance which is in agreement with the maximum power density results shown in Figure 5.a. The increase in temperature also showed an increase in the MEA resistance. Here, the effect of resistance increase was not apparently reflected in the MEA maximum power in Figure 5a. This is due to the contrast in effect of the reduction of mass transport losses and the increase in ohmic losses with increasing the operating temperature. Therefore, the increase in maximum power from 80 °C to 100 °C was due to a significant reduction in mass transport losses which countered the effect of ohmic losses, and then the reduction when increasing the temperature to 120 °C was due to the increase in ohmic losses whilst there was less change in transport losses.

Moreover, it is important to note that the increased in resistance for the composite membranes with increasing temperature is lower when compared to that of recast Nafion, which once again confirms the effect of the increased water retention characteristic of graphene oxide. However, for the 30 μm membranes this was not the case: the recast Nafion actually had a lower resistance than the composite. This could be the result of having a fixed GO loading for all membrane thicknesses and would indicate that there is an optimum GO loading for the different thicknesses which is an area for further investigation.

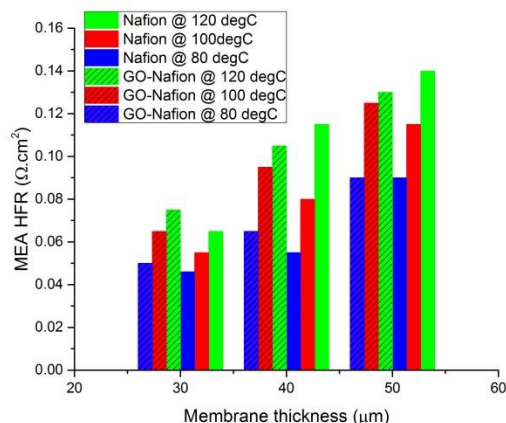


Figure 6: High frequency resistance of the tested MEAs

In Figure 7, the OCV values for the tested MEAs are shown. The recast Nafion results show a significant drop in the OCV values with the temperature increase, and this is more pronounced for the thinner Nafion membranes. In contrast, the OCV for the 40μm and 50μm GO-Nafion composite membranes was almost constant with increasing temperature, and there was a relatively very small drop in OCV for the 30 μm membrane. This demonstrates that the composite membrane is able to maintain low hydrogen crossover through its structure and has higher tolerance to the temperature increase. This can be related to the way the GO sheets are dispersed in the Nafion layer as was shown in Figure 1. The demonstrated stable OCV in the GO-Nafion membranes is an important indication for an increased durability at higher temperatures.

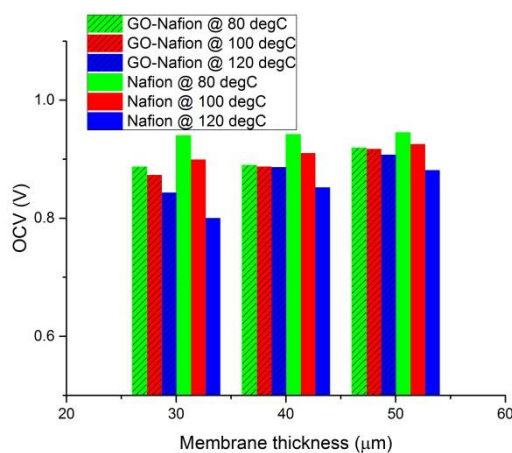


Figure 7: OCV of Nafion and GO-Nafion membranes of different thickness with varying operating temperature.

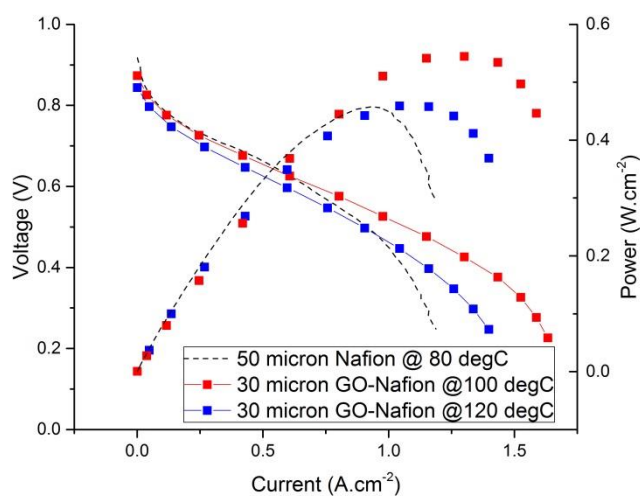


Figure 8: Polarisation and power curves for 50 and 30 micron membranes.

Finally, Figure 8 shows polarisation and power curves of a 50 micron Nafion membrane at 80 °C (presenting the conventionally used membrane thickness) compared to that of a 30 micron composite membrane at 100 and 120 °C (representing the change towards the target membrane). As observed previously, the optimum operating temperature for the fabricated membranes is 100 °C with over 20% performance gain over that of the conventional MEA. Moreover, even at 120 °C the membrane performs better than the 50 micron version at 80 °C. This shows that thin composite membranes have the potential to achieve the targeted operating conditions and performances for the next generation of automotive PEFCs.

Conclusions

Nafion and GO-Nafion membranes were fabricated via solution casting at three different thicknesses. The membranes were characterised and it was confirmed via TGA, SEM and FT-IR that graphene oxide was successfully incorporated into the Nafion structure. The composite membranes exhibited better tensile strength and higher swelling and water uptake, but with lower IEC. In-situ testing revealed that the composite membrane generally had higher performance and potentially better durability.

The increase in temperature up to 120 °C had less of an effect on the performance of the GO-Nafion membranes compared to that of recast Nafion equivalent. The increased water retention properties of the GO-Nafion membranes at elevated temperatures resulted in lower ohmic losses and therefore better performance. Furthermore, this enhanced water uptake in addition to the improved mechanical strength allowed reducing the membrane thickness and improving the performance at elevated temperature whilst maintaining a stable OCV. Moreover, the results presented suggest that

membrane thickness is a significant parameter for consideration when designing and optimising composite membrane materials; a parameter with very little consideration in published literature. This demonstrates the possible higher lifetime of the GO-Nafion composite membranes which will be further examined in future work.

Furthermore, it is especially important to note that the developed GO-Nafion composite membranes were able to demonstrate comparable performance to the conventional membrane at the conventional operating temperature (80°C) while allowing further enhancement in performance at elevated temperatures. In other words, the composite membranes presented here offer an extension of the operating temperature range up to 120 °C, while maintaining the advantage of fast start-up, which is offered by the conventional PEFC system and required for the automotive industry.

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