Effects of Proton Exchange Membrane (PEM) Thickness and Equivalent Weight (EW) on the PEM Fuel Cell Performance at Different Cell Operating Temperatures

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Abstract: The proton conductivity of Nafion 112, 1035, 1135, 115, and 117 membranes has been studied. Measurements were made in 1 M H2SO4 at 298 K using a four-electrode, dc technique. The membrane area resistance increases with thickness, and it was 0.065, 0.092, 0.076, 0.115, and 0.13 Ω. cm^2 for Nafion 112, 1035, 1135, 115, and 117 membranes respectively. The results also showed that the proton conductivity of Nafion 112, 1035, 1135, 115, and 117 membranes was 0.09, 0.11, 0.10, 0.13, and 0.16 S.cm-1 respectively.

In the PEM fuel cell applications, it was observed that the optimum Nafion ionomer wt.% requirement does not change with the membrane thickness and the membrane EW. In addition, the Nafion 1035 membrane can remain hydrated for longer than the Nafion 1135, or Nafion 112 membranes because it's EW is (1000) lower than the Nafion EW of Nafion 1135 (1100), and Nafion 112 (1100). In other words, a higher performance, more stable, and longer life PEM fuel cell can be obtained by using Nafion 1035 membrane as a solid electrolyte especially for high operating temperature.

**تأثيرات سمك غشاء التبادل البروتوني (PEM) والوزن المكافئ (EW)
على أداء خلية الوقود PEM عند درجات حرارة تشغيل مختلفة للخلية**

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ملخص: تم في هذا البحث دراسة الموصلية البروتونيه لأغشية النافيون من نوع 117 ، 115 ، 1135 ، 1035 ، 112 باستخدام تقنية التيار المستمر ذات الأربع أقطاب في وجود 1 M H₂SO₄ عند درجة حرارة 298 K . أظهرت النتائج أن المقاومة السطحية للأغشية تزداد بزيادة سمك الغشاء وكانت قيمتها 0.115، 0.076، 0.092، 0.065، Ω. cm² 0.13 للأغشية 112 و 1035 و 1135 و 115 و 117 على الترتيب. أما الموصلية البروتونية فكانت 0.16، 0.13، 0.10، 0.11، 0.09 S.cm⁻¹ للأغشية 117 و 115 و 1135 و 1035 و 112 على الترتيب. عند استخدام هذه الأغشية في تطبيقات خلايا الوقود تبين ان النسبة الأمثل لعنصر النافيون في طبقة الحافز لا تتأثر بكلا من سمك الغشاء والوزن المكافئ للغشاء. بالإضافة الى أن الغشاء من نوع 1035 يمنح أفضل آداء للخلية في درجات الحرارة العالية لأنه يحافظ على رطوبته لفترة زمنيه أطول من الأغشية الأخرى وذلك بسبب تمتعه بوزن مكافئ أصغر. وبعبارة أخرى يمكن الحصول على خلية وقود ذات غشاء بروتوني أعلى كفاءه وأكثر استقراريه وأطول عمر حتى في درجة حرارة 95 C ° باستخدام الغشاء البروتوني 1035

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Keywords: PEM fuel cells, Proton Exchange Membranes, Nafion Ionomer, Proton conductivity, Renewable Energy.

1. INTRODUCTION

Proton exchange membrane (PEM) fuel cells have been identified as an encouraging technology for a renewable energy source due to advantages such as a lack of pollutant emissions, relatively low operation temperature, and high power density [1,2]. The PEM is the an essential component of a PEM fuel cell, which makes it possible to attain high power densities. It serves as a physical barrier between the anode and cathode gases and also as the electrolyte (hence it known as solid polymer electrolyte). A good membrane material for a PEM fuel cell should have a high ionic conductivity, good chemical and mechanical stability, small water permeability, and low cost. In addition, it should be electronically insulating and not permeable for H_2 and O_2 gases. Nafion is a commercially available perfluorosulfonic cation membrane developed by E.I. DuPont de Nemours & Co. Inc. It is commonly used as the electrolyte in solid polymer electrolyte fuel cells. The structure of Nafion is shown in Figure 1. The values of x and y can be varied to create materials with different equivalent weights (EW). The equivalent weight is defined as the weight of dry polymer in grams containing one mole of exchange sites. The desired equivalent weight is achieved by varying the ratio of vinyl ether monomer to tetrafluoroethylene (TFE). 1100 EW is most commonly used though EWs of 900-1400 are available [3].

Within the family of Nafion, a number such as 117 differentiates the various types of Nafion. The first two digits refer to the equivalent weight of the membrane, e.g. Nafion 1135 has equivalent weight 1100 g/mol. The last two digits refer to the thickness of the membrane in mil (1mil = 0.001 inch = 2.54×10^{-3} cm), e.g. Nafion 1135 has thickness of 3.5 mil. The equivalent weight of the membrane is varied by the changing the length of the backbone, i.e. the value of x, as depicted in Figure 1.

Research on manufacturing and characterizations of Nafion membranes has been reviewed in [4,5].

Proton conductivity of the membrane is particularly important since it plays an important role in controlling the PEM fuel cell performance. High protonic conductivity allows high proton transfer from the anodic reaction zone to the cathode where the oxygen reduction reaction takes place [6]. In the present study, two basic parameters were studied to improve the conductivity of the membranes, the membrane thickness and the membrane equivalent weight (EW).
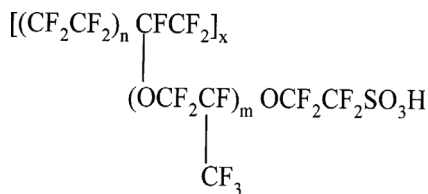
$$[(CF_2CF_2)_n \; CFCF_2]_x$$
$$(OCF_2CF)_m \; OCF_2CF_2SO_3H$$
$$CF_3$$

Figure (1). The structure of Nafion membrane [3]

2. EXPERIMENTAL WORK:

2.1. Membrane Pre-treatment

Before being used in the membrane electrode assembly (MEA), a range of commercially available extruded membranes from DuPont, including, Nafion 112, Nafion 1135, Nafion 115, Nafion 117, and Nafion 1035 with a 3 cm diameter, were washed in various solutions to remove trace of organic and inorganic contaminants and to change their form. The pre-treatment procedure involved boiling the polymer electrolyte membrane in 3 wt.% aqueous H_2O_2 solutions for 1 h at 85-90 °C, followed by boiling for 1 h in deionised water at 85-90 °C, and subsequently boiling for a further 1 h in a fresh sample of deionised water. The membrane was then boiled for 1 h in 0.5 M H_2SO_4 to get a fully H+-form exchanged membrane. After that, the membrane was boiled for 15 min. in pure water at temperature 85-90 oC to remove the remaining H_2SO_4 on the surface of the membrane, followed by storing in fresh deionised water until use.

2.2. Membrane Thickness Measurements

Fresh circular samples of 3 cm diameter were cut from Nafion membranes type 112, 1135, 115, 117 and 1035, for use in membranes' thickness measurements. Both the dry and the hydrated membrane thickness were measured at 20 random points over their surface to ±1 μm using a digital micrometer (Mitutoyo, Digimatic micrometer).

2.3. Proton Conductivity Measurements

The proton conductivity of the proton exchange membranes can be measured by several methods such as ac impedance spectroscopy [7-9], and four-electrode, dc technique [10,15]. Figure 2 shows a photograph of four-electrode, dc technique which is adopted to use in the present study. Two platinum electrodes (as a worked electrodes) were connected to a potentiostat / galvanostat (Autostat, Sycopel), and a waveform generator (PPR1, Hi-Tek) was used to perform linear galvanodynamic current sweeps between 0 and 1000 mA/ cm^2. The tests were run using 1 M H_2SO_4 at temperature of 25 °C. Two saturated calomel reference electrodes (SCE, Radiometer Ref 401, Radiometer, Ltd., Crawley, West Sussex, U.K.) are connected at fixed distance from either face of the membrane using Luggin capillaries and, the potential difference between the SCEs was measured using a high-impedance digital voltmeter (Thandar TM451) connected to the SCEs. The accuracy of placement of the Luggin capillaries was carefully checked by measuring the gap between the Luggin tip and the membrane surface using a vernier gauge. The identical distance of 1.5 mm between the Luggin capillary tip and the membrane surface, with different thicknesses of membrane, was achieved by altering the thickness of the flange gaskets. The details of this technique were published in ref. [10, 15].

The average cell resistance can be determined from the slope of the plotted line which relate the potential difference between the SCEs with the current according to Ohm's law ($\Delta E_{reff}=iR_{Cell}$) (over a wide range of membrane current density. The membrane resistance was then obtained from the cell resistance by measuring the corresponding cell resistance in the absence of the membrane ($\Delta E_{reff}=iR_{reff}$). . This gives the background

electrolyte resistance which is subtracted from the cell resistance to give the membrane resistance (i.e., $R_{membrane} = R_{Cell} - R_{reff}$.) The membrane resistance was then used to calculate the resistivity ($\rho = A R_{membrane}/l_{membrane}$) and the conductivity ($\sigma = 1/\rho$) of the membrane, where $l_{membrane}$ is the membrane thickness, and A is the membrane surface area.
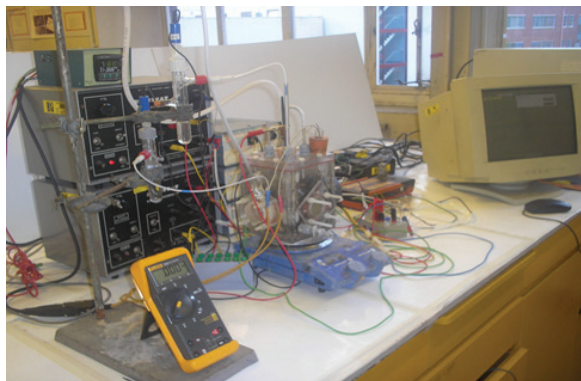

Figure (2). A photograph of four-electrode, dc technique.

2.4. Catalyst Layers Preparation

All of the catalyst layers were prepared in-house by the decals process, with some modifications [11-15]. The catalyst ink was prepared by using of 20 % Palladium supported on carbon catalyst (Pd/C) (supplied by Sigma-Aldrich), and Nafion 20 wt % solution (EW 1000, supplied by Sigma-Aldrich), diluted to 10 wt % in (25 % water, 37.5 % ethanol, and 37.5 % 1-propanol). Catalyst mixtures were prepared in the following way: 3.48 ± 0.1 mg/cm2 of 20 % Pd/C was wetted with a few drops of deionised water, and stirred for 10 min. After stirring, the required volume of 20 wt.% Nafion ionomer solution was added to the mixture and stirred for 30 min, followed by ultrasonication for 1 h. After ultrasonication process, the mixture was kept under stirring overnight to achieve a homogenous ink. The Nafion ionomer loading and the catalyst loading in the catalyst layer can be adjusted, according to the requirements of the parametric study [12]. The formed catalyst ink was brush painted onto a 3.14 cm2 Teflon discs. After painting the decals were left into dry air at room temperature for 30 min., and then weighed. The process of painting and drying was repeated until the desired catalyst loading was reached.

2.5. Membrane Electrode Assembly (MEA)

The membrane-electrode assembly (MEA) was prepared by placing catalyst layers at both sides of the pre-treated Nafion membrane under study, followed by hot-pressing at 140 C and 200 atm for 3 min. The formed MEA's were then hydrated by boiling them in 0.5 M H2SO4 for 1 h, followed by boiling in pure deionised water for 10 min., with excess water subsequently being removed. Finally, the MEA's were placed between two glass strips, which kept it flat while slowly drying prior to use.

2.6. Fuel cell Assembly and Performance Measurements.

PEM fuel cell was assembled by placing the MEA in a single cell test fixture (Electrochem Inc., USA) and connected to fuel cell test station (Nara Cell Tech Corp., Korea) provided with gas humidifier, mass flow controller, temperature indicator-controller etc. The current–voltage (*i*–V) characteristics of the cell was evaluated, using hydrogen and oxygen reactants at 1 atm, at 85°C using HPCS1 high power potentiostat/glvanostat along with WBCS3000 battery cycler system

3. RESULTS AND DISCUSSION

3.1 Membrane Thickness

Table 1, shows the nominal (as supplied), dry, and hydrated thickness for the range of Nafion membranes measured using the micrometer. In the case of the hydrated thickness, In the case of the membrane thickness in the MEAs, the results of the SEM measurements are published by the authors in ref. [13] and also presented in Table 1.

Table (1). Membrane thickness measurements

Nafion Membrane Type (μm)	Thickness as Supplied (μm)	Measured Thickness (μm)	Hydrated Thickness (μm)	Dried Membrane Thickness (μm)	SEM Membrane Thickness (μm) [13]
112	51	50 ± 1	59 ± 2	51 ± 1	41 ± 2
1035	89	89 ± 2	105 ± 3	90 ± 1	85 ± 3
1135	89	90 ± 1	108 ± 2	91 ± 1	76 ± 3
115	127				---
117	178				--

The results show that the Nafion membranes volume was swelled in the X-Y-Z plane. The membrane thickness was increased by 15 to 20 % after the hydration. Therefore, in the measurements of the membrane resistivity and conductivity we should use the hydrated thickness instead of using dry or nominal thickness of the membranes. When the membranes were dried again for 48 h in an oven at 60 ºC, the thickness measurement results, which are presented in Table 1, showed good agreement with the dried membrane thicknesses before the membrane treatments.

3.2 Proton Conductivity

Proton conductivity of Nafion membranes is complex due to its dependence of hydration, pretreatment process, and operating temperature. Figure 3, illustrates the variation of area resistance with hydrated membrane thickness for Nafion 112, 1135, 115, and 117. The Nafion 1035 not included in this section because the EW need to be fixed in order to study the effect of membrane thickness. The results showed that the area resistance increases as the membrane thickness is increased.
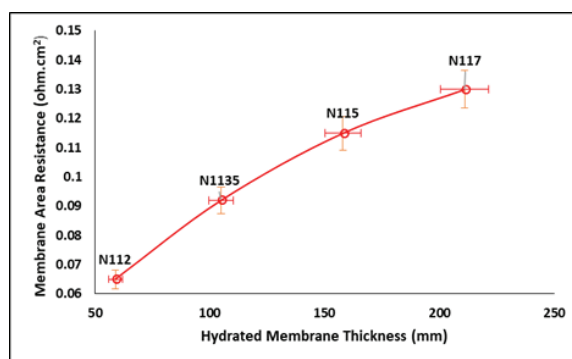
Figure (3). Variation of membrane resistance area with the membrane thickness.

Figures 4, shows the variation in the conductivity and of the Nafion membranes under study with hydrated membrane thickness in 1 M H_2SO_4 at 25 °C respectively. The Nafion membranes do not show such independence under the experimental conditions. The lower conductivity and higher resistivity of the thinner Nafion membrane materials is clear. A series of experiments made by Slade *et.al.*, [10] to measure the proton conductivity of Nafion 117, and Nafion 112 in _1 M H_2SO_4 at 298 K using a four-electrode, dc technique.
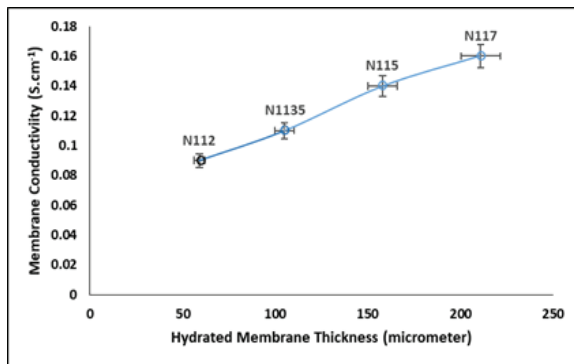

Figure (4). Variation of membrane conductivity with the membrane thickness.

The membrane resistance area was found from 0.07 Ω.cm2 for Nafion 112 and 0.16 Ω.cm2 for Nafion 117. Moreover, the membrane conductivity was found from 0.083 S.cm-1 for Nafion 112 and 0.16   S.cm^{-1} for Nafion 117. The results are in good agreement with the values reported by Slade et al. [6]. For the Nafion 1035, the resistance area, resistivity, and conductivity are 0.092 Ω. cm2, 8.76 Ω. cm, and 0.11 S.cm-1 respectively. Table 2. presents the measured resistance area, resistivity, and conductivity of 112, 1035, 1135, 115, 117 Nafion membranes.

Table (2). the measured resistance area, resistivity, and conductivity of Nafion 112, 1135, 1035, 115, and 117 membranes

Membrane Type	Resistance Area (Ω. cm²)	Resistivity (Ω. cm)	Conductivity (S.cm^{-1})
112	0.065	11.01	0.09
1035	0.092	8.76	0.11
1135	0.076	9.3	0.10
115	0.115	7.28	0.13
117	0.13	6/16	0.16

3.3 Polarization Curve

3.3.1 Membrane Thickness Effect.

PEM Fuel cell catalyst layers with a palladium loading of 3.48 ± 0.1 mg/cm² of 20 % Pd/C were prepared with different Nafion ionomer (EW 1000) weight percentage ranging from 20 to 45 wt.% and assembled with Nafion 112 membrane to form membrane electrode assembly (MEA). The cells performance was evaluated at 85 ˚C, with humidified hydrogen-oxygen reactants, at 1 atm. pressure.

Figure 5, illustrates the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of 3.48 ± 0.1 mg/cm^2 and different Nafion ionomer contents, ranging from 20 to 45 wt.%, with humidified hydrogen-oxygen reactants at 85 ˚C, temperature and, 1 atm pressure. The best performance is obtained at 30 wt.% Nafion loading for catalyst layers with 3.48 ± 0.1 mg/cm^2 of 20 % Pd/C. The same specifications catalyst layers were also prepared, and assembled with Nafion 1135, 115, and 117 and tested to study the influence of optimum Nafion ionomer wt.% requirement in the catalyst layers by the membrane thickness. Figure 6, shows the effect of Nafion ionomer wt.% loading on the catalyst layer performance using Nafion 112, 1035, 1135, 115, and 117 as a membrane.
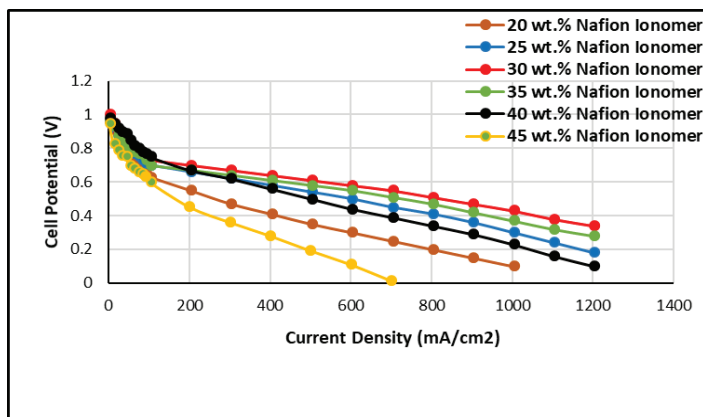

Figure (5). the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of 3.48 ± 0.1 mg/cm^2 and different Nafion ionomer contents, ranging from 20 to 45 wt.%, with humidified hydrogen-oxygen reactants at 85 ˚C, temperature and, 1 atm pressure.
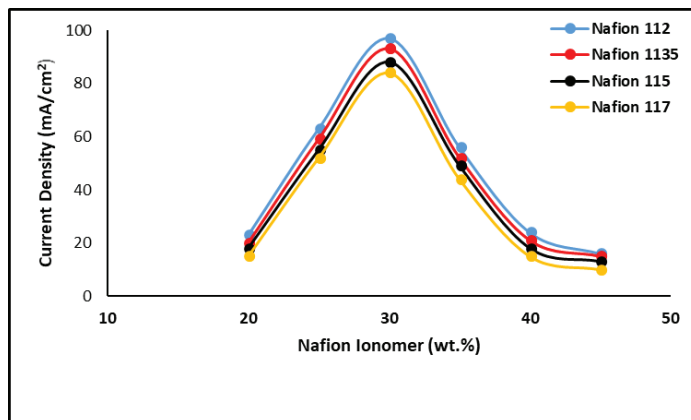

Figure (6). the effect of Nafion ionomer wt.% loading on the catalyst layer performance using Nafion 112, 1135, 115, and 117 as a membrane

The result shows that the best performance is obtained at 30 wt.% Nafion loading for catalyst layers with 3.48 ± 0.1 mg/cm^2 of 20 % Pd/C catalyst loading. Therefore, the optimum Nafion ionomer wt.% requirement does not change with the membrane thickness. However, higher current density obtained with the 112 membrane may be attributed to the higher protonic conductivity of the 112 membrane than that of the other membranes.

3.3.2 Membrane Equivalent Weight (EW) Effect

Catalyst layers with the same specifications as in section 3.3.1, were used to study the effect of the Nafion membrane EW on the optimum Nafion requirement for high MEAs performance. The catalyst layers were assembled with 1035 Nafion membrane and the MEAs performance was compared with the performance of catalyst layers assembled with 1135 membranes. Figure 7, illustrates the effect of Nafion ionomer wt.% loading on the catalyst layer performance using Nafion 1035 and 1135 as a membrane. From the figure, it can be seen that, the best performance is obtained at 30 wt.% Nafion loading, for MEAs using 1035 Nafion membranes which is the same as that of using Nafion 1135 membranes. Thus, the optimum Nafion ionomer wt.% in the catalyst layers   does not change with the equivalent weight of the Nafion membrane used but, higher current density obtained with the 1035 membrane.
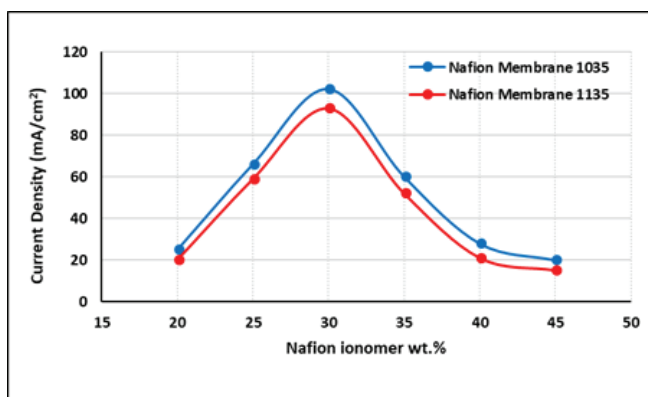

Figure (7). the effect of Nafion ionomer wt.% loading on the catalyst layer performance using Nafion 1035 and 1135 as a membrane.

3.3.3 The Cell Operating Temperature effect

The effects of the operating temperature on the PEM fuel cell performance were studied by assembling catalyst layers of 3.48 ± 0.1 mg/cm^2 of 20 % Pd/C catalyst loading and 30 wt.%. Nafion ionomer loading with Nafion 1035, Nafion 1135, and Nafion 112 membranes at 85 °C, with humidified hydrogen-oxygen reactants, at 1 atm. pressure and the results are presented in Figure 5. The results showed that, at low current densities there is big difference between the membranes. However, at high current densities the best performance was achieved by of the PEM fuel cell containing Nafion 1035 Nafion membrane. These results clearly show a decrease in the membrane conductivity as the membrane thickness is reduced and the lower EW membrane performance in PEM fuel cell is much better than the higher one. In the same manner, the same tests were performed at 95 °C, with humidified hydrogen-oxygen reactants, at 1 atm. pressure as operating conditions and the results are presented in Figure 6. The results showed that, the PEM fuel cell containing Nafion 1035 Nafion membrane performance is higher and more stable at high temperature than that of the PEM fuel cell containing Nafion 112, and 1135 Nafion membrane. Other factors such as the catalyst layer structure, should be taken into account. In addition, the Nafion 1035 membrane can remain hydrated for longer than the Nafion 1135, or Nafion 112 membranes because it's EW is (1000) lower than the Nafion EW of Nafion 1135 (1100), and Nafion 112 (1100). Since the protonic conductivity of Nafion membranes is inversely proportional to their EW. Therefore, a higher performance, more stable, and longer life PEM fuel cell can be obtained by using Nafion 1035 membrane as a solid electrolyte.
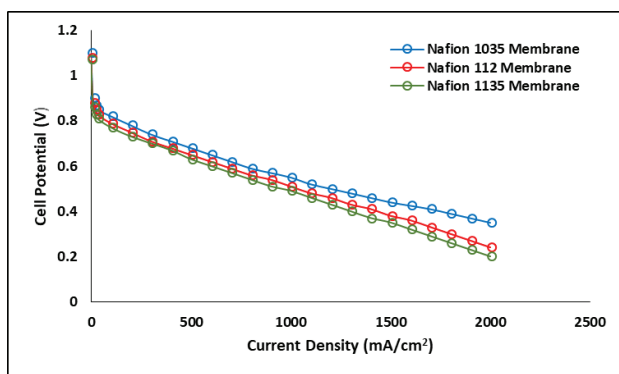
Figure (8). the current-voltage (i-V) characteristics of the catalyst layer with Pd/C of 3.48 ± 0.1 mg/cm^2 and 30 wt.% Nafion ionomer (EW1000) contents, with Nafion 1035, Nafion 1135, and Nafion 112 membranes at 85 ˚C, with humidified hydrogen-oxygen reactants, at 1 atm. pressure.

4. CONCLUSION

The proton conductivity of the membrane is particularly important since it plays an important role in controlling the PEM fuel cell performance. High protonic conductivity allows high proton transfer from the anodic reaction zone to the cathode where the oxygen reduction reaction takes place. Based on the results of this study it can be conclude that:

- The membrane area resistance increases with thickness, and it was 0.065, 0.092, 0.076, 0.115, and 0.13 Ω. cm^2 for Nafion 112, 1035, 1135, 115, and 117 membranes respectively.

- The proton conductivity of Nafion 112, 1035, 1135, 115, and 117 membranes was 0.09, 0.11, 0.10, 0.13, 0.16 S.cm^{-1} respectively.

- the optimum Nafion ionomer wt.% requirement does not change with the membrane thickness and the membrane equivalent weight (EW).

Finally, a higher performance, more stable, and longer life PEM fuel cell can be obtained by using Nafion 1035 membrane as a solid electrolyte especially for high operating temperature.
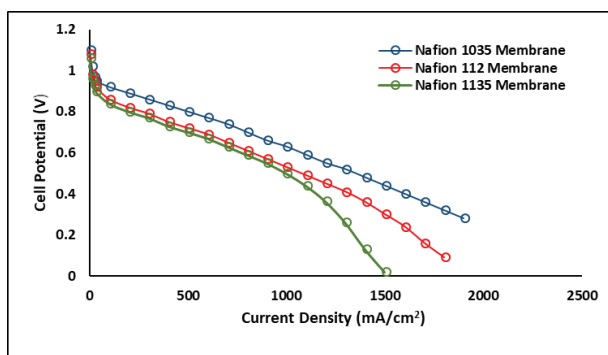

Figure (9). The current-voltage (i-V) characteristics of the catalyst layer with Pd/C of 3.48 ± 0.1 mg/cm^2 and 30 wt.% Nafion ionomer (EW1000) contents, with Nafion 1035, Nafion 1135, and Nafion 112 membranes at 85 ˚C, with humidified hydrogen-oxygen reactants, at 1 atm. pressure.

REFERENCES

[1]. Yuan X, Wang H. PEM fuel cell electrocatalysts and catalyst layers. London: Springer; 2008.

*[2]. K.A. Carrette, K.A Friedrich, and U. Stimming: "Fuel cells- fundamentals and applications", Fuel Cells, **1**, (1), pp. 5. 2001.*

[3]. T. D. Gierke, G. E. Munn and F. C. Wilson. "Morphology of perfluorosulfonated membrane products." ACS Symposium Series, 180, pp.195. 1982.

*[4]. K. D. Kreuer; "On the Development of Proton Conducting Polymer Membranes for Hydrogen and Methanol Fuel Cells." Journal of Membrane Science, **185**, (1), pp.-29, 2000.*

[5]. K. D. Kreuer, "On the development of proton conducting materials for technological Applications" Solid State Ionics, 97, (1), pp.1. 1997.

[6]. M. Laporta, M. Pegoraro, and I. Zanderighi: "Perfluorosulfonated membrane Nafion: FT-IR study of the state of water with increasing humidity", Physical Chemistry Chemical Physics, 1, pp.-4619.

[7]. S. Gottesfeld and M. Wilson, Thin film catalyst layers for polymer electrolyte fuel cell electrodes. Journal of Applied Electro-chemistry, 22, (1), pp 1, 1992.

[8]. [132]   T. E. Springer, M. S. Wilson, and S. Gottesfeld; "Modelling and experimental diagnostics in polymer electrolyte fuel cells", Journal of the Electrochemical Society, 140, (12), 1993, pp. 3513

[9]. S. Gottesfeld and M. Wilson: " High performance catalyzed membrane of ultra-low Pt loading for polymer electrolyte fuel cells"., Journal of the Electrochemical Society, 139, (1), pp. L28. 1992.

*[10]. S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh:" Ionic Conductivity of an Extruded Nafion 1100 EW Series of Membranes", Journal of The Electrochemical Society, **149** (12), A1556, 2002.*

[11]. Z. Qi, and R. Kaufman: "Low Pt loading high performance cathodes for PEM fuel cells", Journal of Power Sources, 113, (1), pp. 37, 2003.

[12]. A. A. Sghayer, A. Diyaf, K. A. Mazuz, and N. A. Issa:" The Effect of Nafion Ionomer Equivalent Weight (EW) on Polymer Electrolyte Membrane Fuel Cell Catalyst Layer Performance", in press 2020.

[13]. A. A. Sghayer, K.A. Mazuz, K.M. Etmimi, R. M. Said, A. A. Ewhida: " Some Membrane Parameters Affecting the PEM Fuel Cell Performance", Libya for Applied and Technical Science, Vol 2, Issue 1, pp. 1 ,2013.

[14]. H. L. Yeager, in Perflourinated Ionomer Membranes, A. Eisenberg and H. L. Yeager, Editors, ACS Symposium Series 180, American Chemical Society, Washington, DC 1982.

[15]. S. Gottesfeld and T. A. Zawodzinski, in Polymer Electrolyte Fuel Cells, Advances in Electrochemical Science and Engineering, Vol. 5, pp. 245, Wiley, New York 1997.