ASSESSING THE ELECTRICAL CONDUCTIVITY OF BENZENE SOLFUNICAS AN ELECTROLYTE FOR FUEL CELLS MEMBRANES` IN HIGH AND LOW OPERATING TEMPERATURES

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Abstract

Nafion and PA doped PBI membranes have been considered to be the most promising membranes for low and high temperatures PEMFC, respectively. However, there have been some limitations for them. Nafion's membranes could suffer catalyst deactivation and water flooding at the cathode side. On the other hand, PA doped PBI struggle low oxygen solubility; strong phosphate anion adsorption on the catalyst surface. This research was to test the electrical conductivity of BSA doped PBI membrane in low and high operating temperatures for fuel cells.

The electrical conductivity tests were conducted by the two Pt probe technique. The electrical conductivity of BSA doped PBI membranes were very weak (0.0005S.cm^{-1}) at high temperatures > 100^{o}C compared to PA doped PBI membrane. In contrast, BSA doped PBI membrane performed higher electrical conductivity than H_3PO_4 doped PBI membrane and Nafion's membranes at low temperatures (40-80^{o}C). This was proved with 0.28372 S.cm^{-1}at 40^{o}C for BSA doped PBI higher than 0.05681S.cm^{-1}at 80^{o}C for Nafion's membranes and 0.038S.cm^{-1} at 140^{o}C for PA. The promising high electrical conductivity of BSA doped PBI membranes at low temperatures in comparison of PA and Nafion's membranes encourages conducting further future studies to test oxygen reduction reactions and to perform I-V polarizations in order to evaluate its electrical power output.

Keywords: Organic acids; PBI membranes; Nafion membranes; proton conductivity.

Nomenclature

PEMFC: Polymer Electrolyte Membrane Fuel Cells
PBI: Polybenzimidazole
PRU: Per repeated unit of PBI
PA: Phosphoric acid
σ:electrical conductivity
PEM: Polymer Electrolyte membrane
X: Doping level
BSA: Benzene sulfonic acid
R: electrical resistance
T_H: Humidifier temperature, ^{o}C

A: membrane`s cross sectional area **L**: Thickness of membrane

Introduction

In literature, there have been two models to explain proton conduction mechanism in an electrolyte solution. (Kreuer, K. D., 1997), called the first approach as the Grotthuss mechanism; it considerers the water as the best solvent for protons, it is also referred to as the hopping mechanism. This model shows that proton conduction involves rapid transfer of intermolecular protons through a chain of hydrogen bonds. It assumes that transfer activities are closely related to each other; the water dipoles are re-orientated to form an arrangement that will ease the accommodation of the following hopping event. The second model was proposed by (Kreuer et al., 1992) and they referred to as the vehicle mechanism or molecular diffusion. In this model, they studied the proton conductivity of some fast proton conductors such as zeolites, Nafion, etc. This model assumed that the protons are not transferred as H^+ but as H_3O^+, NH_4^+, etc.; they attach themselves to carriers such as H_2O, NH_3 etc. The carriers to which protons do not bond with will migrate in the reverse direction.

According to (Ma et al., 2004) one of the most traditional membranes that have been used for low temperature PEMFC is Nafion® (Du Pont Inc.). The presence of per fluorinated chain in Nafion membrane offers good chemical and mechanical stability below 90^{o}C. In addition, it has a high conductivity (>0.05 S.cm^{-1} at room temperature and 100% relative humidity). However, the conductivity of Nafion depends greatly on its water content. The Operating temperatures of Nafion based membranes are limited between 50 and 90^{o}C. Another issue for low temperature fuel cells is water flooding at the cathode due to the accumulation of excess water that causes oxygen mass transfer limitations. According to (Lobato et al., 2007), the presence of poisonous chemicals such as CO and H_2S in the fuel has a negative impact on the performance of low temperature fuel cells due to catalyst deactivation.

(Hogarth and Glipa, 2001) devised two ways to overcome the decrease in conductivity in polymer base electrolytes at high temperatures. The first approach is based on using polymer systems that are tolerant against dehydration or those that are able to exhibit good conductivity at low levels of hydration and only operate below 150^{o}C. The second approach is based on using anhydrous polymer systems in which proton transfers are not carried by water and they are able to operate at temperatures higher than 150^{o}C.

According to (Scott K, 2007; Li Ma, 2008; Kongstein, 2007; and Hogarth, 2001), to overcome the above mentioned limitations for low temperature PEMFC, the operation temperature of PEMFC needs to be increased. The high operating temperature PEMFCs has the following advantages: higher CO tolerance in the feed gas, enhanced reaction kinetics on both of anode and cathode, use of non-noble

catalyst, use of simpler cooling systems and less complicated integrated reformer systems.

According to (Kongstein, 2007; and Hogarth, 2001), one of the most promising proton exchange membranes that operate at high temperature (more than 100^{o}C) is Polybenzimidazol (PBI) is doped with phosphoric acid. PBI has been used as a fire resistant fabric for fire fighters clothes for its high thermal stability.

Figure (1) shows the chemical structure of PBI and Table (1) shows the proton conductivity properties of PBI membrane. (Wainright et al., 1995) were the first who introduced the approach of using phosphoric acid doped PBI. Operating PBI based fuel cells at temperatures of 185^{o}C leads to CO tolerance up to 3%.

Table (1): Proton Conductivity of Pristine PBI Membrane at Room Temperature (Radev et al. 2008).

Conductivity (S/cm)	Medium	Reference
2.85×10^{-7}	PBI with nominal moisture	[25]
$2 - 8 \times 10^{-4}$	0-100% RH	[26]
10^{-10} to 10^{-9}	In various acid solutions	[27]
6.3×10^{-3}	Aqueous HCl solution (4mol/dm^3)	[1]
1.6×10^{-4}	Aqueous H_3PO_4 solution (6mol/dm^3)	[1]

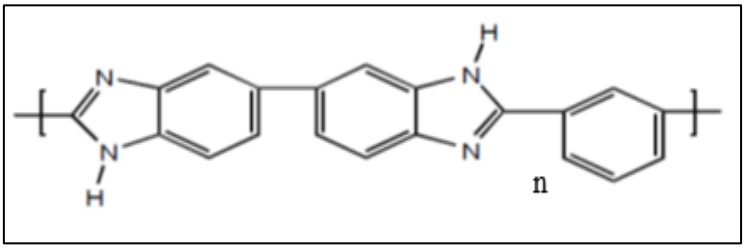


Figure (1): Molecular Structure of Polybenzimidazol (Radev et al., 2008).

(Scott K, 2007) stated that the electrical conductivity for PBI in its pure state is very low (10^{-12} S.cm^{-1}). In regard to (Robert N, 1980), an effective way to substantially increase the electrical conductivity of PBI is by doping it with different acids. Sulfuric acid, phosphoric acid, perchloric acid, nitric acid and hydrochloric acid all have been used to dope PBI. (Ma, 2004) considered phosphoric acid to be the most promising acid due to its 3-D hydrogen bonding network, high thermal stability as

well as its high electrical conductivity at elevated temperatures and its lower volatility at temperatures above 150^{o}C.

Despite, the improvements of using phosphoric acid in doping PBI, the main remaining limitations are: loss of the acid through vapor exhaust and fuel gas streams, low electro catalyst activity and strong adsorption of phosphate anions on the platinum catalyst surface combined with oxygen low solubility and sluggish oxygen reduction reactions (Scott K, 2010).

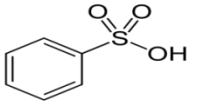
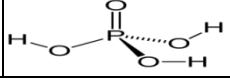
Due to the above mentioned limitations of Nafion and PA doped PBI membranes at low and high operating temperatures in PEM fuel cells respectively, this research is to investigate the electrical conductivity performance of the proposed organic acid (Benzene sulfonic acid). It is also to compare its electrical conductivity performance by using the Nafion's membranes in low temperature fuel cells operating conditions and by using PA doped PBI membrane`s in high temperatures fuel cells operating conditions.

Methodology

Proposed Organic Acid to be Doped with PBI Membranes

After a deep search in organic acids that have similar physical and chemical properties to phosphoric acid in terms of (boiling and melting points) as showed in Table (2). Benzene sulfonic acid was among of the organic acids group to be doped in PBI fuel cells membranes in order to investigate its electrical conductivity performance at low and high temperatures PEM fuel cells conditions. This could lead to comparing its electrical conductivity with Nafion membranes in low temperatures PEM fuel cells and with PA doped PBI membranes in high temperature PEM fuel cells.

Table (2): Chemical and Physical Properties of Benzene Sulfonic Acids Comparing to Phosphoric Acid (Material and safety data sheets for phosphoric and benzene sulfonic acids. 2020).

Acid	Chemical formula	Chemical structure	Molecular weight, g/mole	Boiling point, ^{o}C	Melting point, ^{o}C	Density, gm/cm^3	Vapour pressure Pa at 20^{o}C	Solubility in water,
BSA	$C_6H_6O_3S$		158.2	190	51	1.3	N.A	93mg/100ml At 20^{o}C
PA	H3PO4		98	213	42	1.9	4	Very good

Preparing Benzene Sulfonic Acid Doped PBI Membranes

Three aqueous solution samples of benzene sulfonic acid (5, 6 and 7M) were prepared and put in bottles of 20 ml size. A fourth sample of 11M phosphoric acid was prepared and put in a 20ml bottle too. Figure (2) shows a cut piece of PBI membrane doped in a 20ml bottle of 7M benzene sulfonic acid.

Four PBI membranes of (1cm×2cm) were cut from 40 μm thickness PBI membrane sheet and each was doped with the concentration of BSA, later they were used for conductivity measurements. Before doping any PBI membranes with any organic acid solution, the (1cm×2cm) PBI membranes had been weighed and recorded as (W_1). In addition, the thickness of the above membranes was recorded. Afterwards, these PBI membranes were doped with benzene sulfonic acid for at least 7 days. After doping with an organic acid, the weight of the (1cm×2cm) PBI membrane was recorded as W_2.

Figure (2): A PBI Membrane Doped in 7 M BSA Solution.

Measuring Doping Levels of Acids Doped PBI Membranes

According to (Qingfenget et al., 2000), One of the important factors of proton conductivity is doping level which is the ratio of moles of the acid doped in the PBI membrane to the repeated moles of PBI membrane. Therefore, an initial indicator step for measuring proton conductivity was calculating doping levels of the organic acid in PBI membranes. In one sample, the initial weight of (2cm×2cm) PBI membrane before doping it in 7M solution of benzene sulfonic acid was 0.0269 g. The weight of the same membrane after doing it with the same solution for 17 days was 0.1345 g. The weight of benzene sulfonic that was adsorbed in the above membrane is = 0.1345 – 0.0269 = 0.1076 gm.

Number of moles of PBI membrane before doping = 0.0269(gm)/308.336 ($gm.mol^{-1}$) = 8.72425×10^{-5} moles.

Number of adsorbed moles of benzene sulfonic acid in PBI membrane = 0.1076/158.2 = 6.8×10^{-4} moles

Doping level of an acid doped PBI membrane was calculated as follows:

$$\textbf{Doping level, PRU} = \frac{\textbf{moles of an absorbed acid by PBI membrane}}{\textbf{moles of PBI membrane before doping it}}$$

Therefore, doping level of 7M benzene sulfonic acid = $\frac{6.8\times10^{-4}}{8.72425\times10^{-5}} = 7.79$ per repeating unit (PRU)

Doping level calculations for all benzene sulfonic acid solutions and phosphoric acid doped PBI membranes were carried out in the same manner explained above**.**

Electrical Conductivity Test Measurement

A two Platinum (Pt) probe technique was used to measure the electrical conductivity of the organic acid doped PBI membranes. Figure (3) shows how to place the doped membrane on the two (Pt) probe inside half cell of the proton conductivity testing cell. Meanwhile, Figure (4) shows the whole required apparatus system for this technique. It consists of the Frequency Response Analysis (FRA) (Voltech TF, 2000, UK) that applies AC impedance frequency in the range between 1 kHz and 20 kHz, a voltmeter, an ampmeter, temperature controllers, a humidifier, a humidity sensor, a testing cell and a torque wrench.

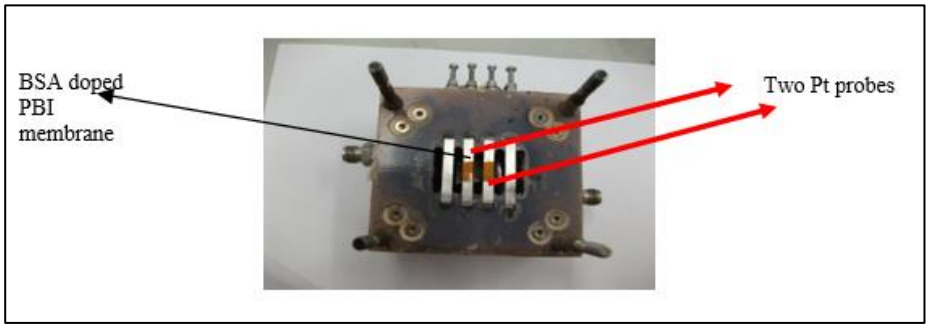


Figure (3): The Half Cell of the Proton Conductivity Testing Cell.

To calculate the cross sectional area of the membranes, the thickness of PBI membranes before and after doping them with the doping acids must be measured. Once the doped PBI membranes was placed on two platinum (Pt) probes with spacing of 0.5cm of a cell test as shown in Figure (4), the testing cell was closed and torqued. Then, the testing cell was connected to the Ampmeter, voltammeter and

Frequency Response Analysis FRA. After that, the testing cell was heated between 80 and 200^{o}C with 20C intervals. For example, 80, 100, 120, etc... At each temperature interval the cell had to be kept for 20 minutes at that temperature in order to get a steady temperature.

The FRA was used to apply AC impedance frequency (from 1 kHz to 20 kHz), then current and voltage readings were recorded using the voltammeter and ampmeter in order to calculate the electrical resistance (R) and proton conductivity (σ) at that temperature. Afterwards, the maximum value of proton conductivity among various frequencies reading was selected as the right value of proton conductivity at that temperature. Finally, a temperature vs. conductivity plot was drawn at different concentrations to compare it with the benchmark plot of phosphoric acid doped PBI membranes and Nafion membranes. Equations (1) and (2) was used to calculate the electrical resistance (R) and electrical conductivity (σ)

Electrical Resistance, R= Voltage(V)/Current (I) ……(1)

Electrical proton conductivity (σ) = 1/R*(L/A) ……..(2)

Where:

A=Cross-sectional Area of the membrane.

L=thickness of the membrane.

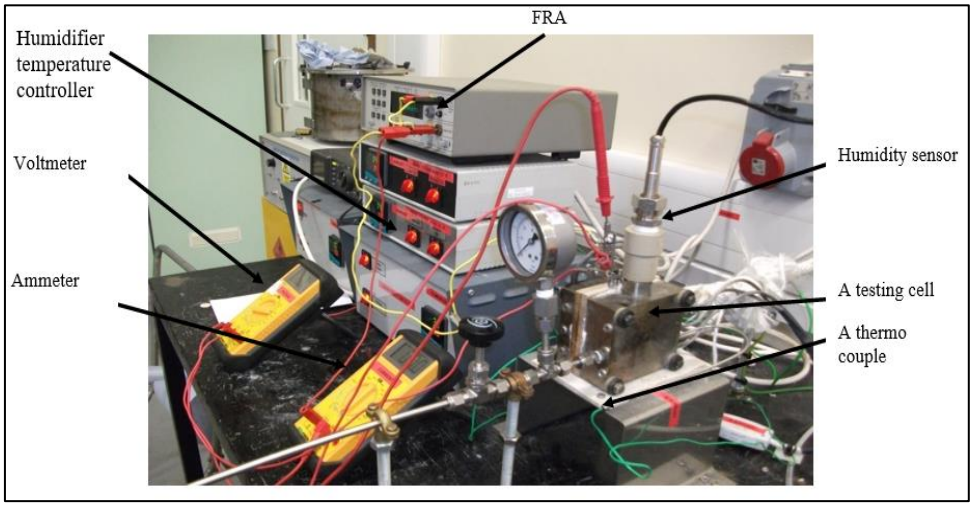


Figure (4): Proton Conductivity Set-Up Equipments.

Results and Discussions

Table (3) shows that the doping level of the adsorbed acid in the PBI membrane goes up with increasing the doping time and the concentration of acid solution used to dope the membrane. On the other hand, Table (4) shows a sample of the recorded voltages, currents and the calculated electrical conductivity for 7M BSA doped PBI membrane.

It can be seen from this table that the maximum value of proton conductivity$\sigma = 8.33\times10^{-2}$(S/cm**)**at 80**º**C. The other measured electrical proton conductivity tables for other concentrations of BSA and PA doped PBI membranes at different temperatures will be put in an appendix for this research.

Table (3): Doping Time and Doping Level of PBI Membranes Doped in Benzene Sulfonic Acid and Phosphoric Acid.

Acid	Concentration	Doping time	Doping level.
Benzene sulfonic acid	5M (water)	15 days	5.58 PRU
	6M(water)	16days	6.44 PRU
	7M(water)	17days	7.79 PRU

Figure (4) shows the proton conductivity of various doping levels of benzene sulfonic acid doped PBI membranes as a function of temperature. This figure reveals undesirable behavior of proton conductivity of BSA doped PBI membranes which are represented in lower proton conductivities at higher temperatures in the range between 100 and 180^{o}C. In addition, another surprising fact was revealed from this figure that the conductivity of this acid doped PBI membrane decreased as doping level was raised. The reason behind the above detrimental performance of BSA doped PBI conductivity at high temperature could be due to the decomposition of the BSA which had been proved by changing the color of the BSA PBI membrane from reddish brown before testing to blackish brown after testing. This behavior was recorded by (Robert et al., 1980) where they found out that the BSA solution experienced decomposition at high temperatures turning its colour from light brown into black in the presence of the Pt-black electrode.

Table (4): A Calculated Sample for BSA Doped PBI Membranes Conductivity Data Test for (x = 7.79PRU).

Testing temperature (80°C), T_H = 50°C, membrane thickness before doping = 40µm and after doping = 87 µm						
Frequency (kHz)	**Voltage (mV)**	**Current (µA)**	**Resistance (Ω)**	**Length(cm)**	**Area, A(cm^2)**	**σ(S/cm)**
20	1.2	3.8	315.7895	0.5	0.019	**8.33E-02**
16.1	30.6	49.3	620.6897	0.5	0.019	4.24E-02
13.1	47.8	57.5	831.3043	0.5	0.019	3.17E-02
10.5	45.6	52	876.9231	0.5	0.019	3.00E-02
8.58	41.7	46.7	892.9336	0.5	0.019	2.95E-02
6.89	39.3	43.4	905.53	0.5	0.019	2.91E-02
5.58	40	42.4	943.3962	0.5	0.019	2.79E-02
4.48	40.6	41.1	987.8345	0.5	0.019	2.66E-02
3.65	41.3	39.7	1040.302	0.5	0.019	2.53E-02
2.92	42.1	38.5	1093.506	0.5	0.019	2.41E-02
2.38	42.9	37.4	1147.059	0.5	0.019	2.29E-02
1.9	44.1	36.1	1221.607	0.5	0.019	2.15E-02
1.55	45	35	1285.714	0.5	0.019	2.05E-02
1.24	46.3	33.7	1373.887	0.5	0.019	1.92E-02
1	47.3	32.6	1450.92	0.5	0.019	1.81E-02

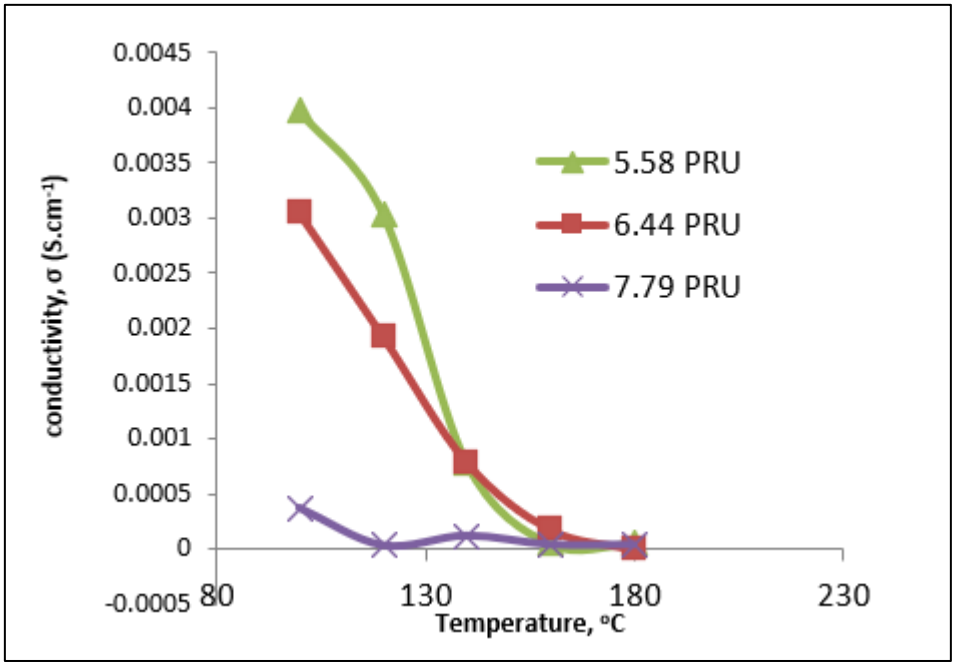


Figure (5): The Electrical Conductivity of BSA Doped PBI Membranes and Doping Levels at High Temperatures.

On the other hand, Figure (5) compares conductivity performance of phosphoric and benzene sulfonic acids doped PBI membranes at high temperature (100 – 180^{o}C). This figure reveals that conductivity performance of PA doped PBI membranes was significantly greater than BSA doped PBI membranes. This poor electrical conductivity performance of BSA doped PBI membranes at high operating temperatures can be attributed to the decomposition of the BSA in the membrane as stated earlier. Therefore, it was suggested to investigate the conductivity behavior of BSA doped PBI membranes at low temperatures (40 – 80C).

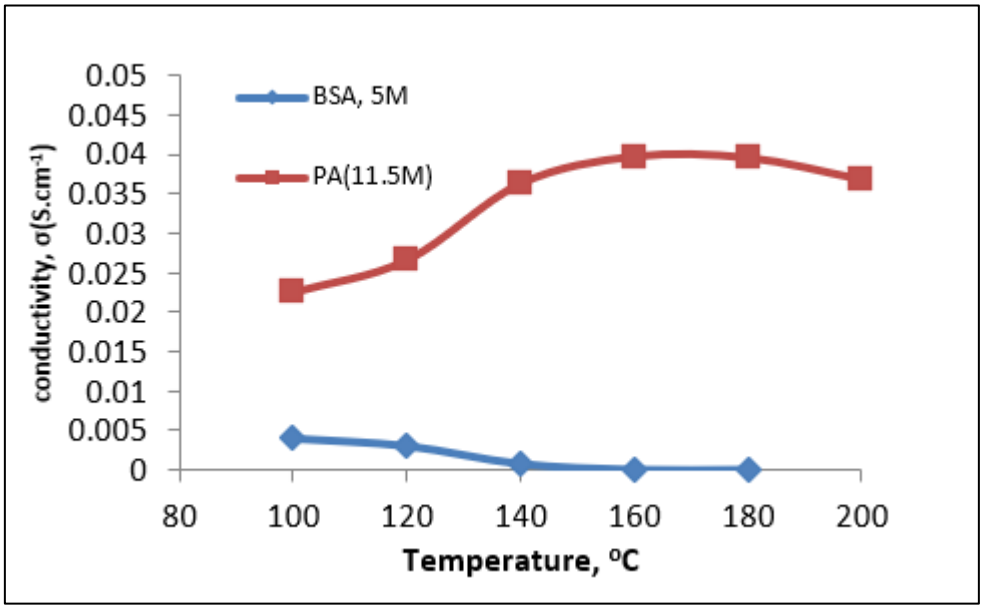


Figure (6): Conductivity Comparison of PSA and PA at High Temperatures.

Figure (7) reveals that the conductivity of BSA doped PBI membranes was significantly higher at low temperatures (40 – 80^{o}C) than high temperatures (100 – 180^{o}C), particularly at (40^{o}C, 7.79 PRU, humidifier temperature, T_H = 40^{o}C) about 0.28379 S.cm^{-1}. This value was even higher than the recorded conductivity by (Radev et al., 2008) for Nafion hydrated membranes (0.089 and 0.059 S.cm^{-1}) with thicknesses of 210×10^{-4}, 110×10^{-4} cm, respectively at 80^{o}C and 100% RH. In addition, it can be seen from figure 8 that at temperature of 70^{o}C (T_H = 40^{o}C), the conductivity of BSA doped PBI (7.79PRU) is almost 0.1S.cm^{-1} which is higher than even the measured conductivity by (Li et al., 2004) for the commercial Nafion NRE 211 about (0.05681 S.cm^{-1}) and Nafion® 117 around 0.068 S.cm^{-1} at (80% RH and 80^{o}C as showed in Figure (8). In comparison with H_3PO_4 doped PBI membranes, conductivity of BSA doped PBI membrane at (70^{o}C, TH = 40^{o}C) around 0.1S.cm^{-1} was greater than that of H_3PO_4 doped PBI membranes about 0.038 S.cm^{-1} at (140^{o}C and 10%RH) as showed in Figure (8).

The high value of BSA doped PBI conductivity at low temperatures might be due to the presence of sulfonated groups on the acid structure, higher stability at lower temperatures due to avoiding hydrolysis and decomposition and higher water content at temperatures below 100°C. Therefore, it was suggested to compare BSA doped PBI with Nafion 112 performance at low temperatures in terms of oxygen reduction reaction kinetics and fuel cells polarization curves for further future studies.

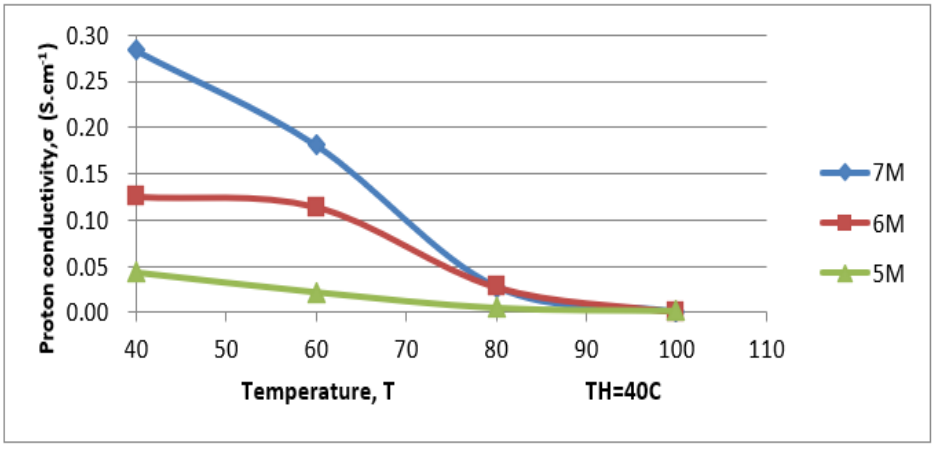


Figure (7): BSA Doped PBI Membranes Conductivity Variation with Doping Levels at Low Temperatures.

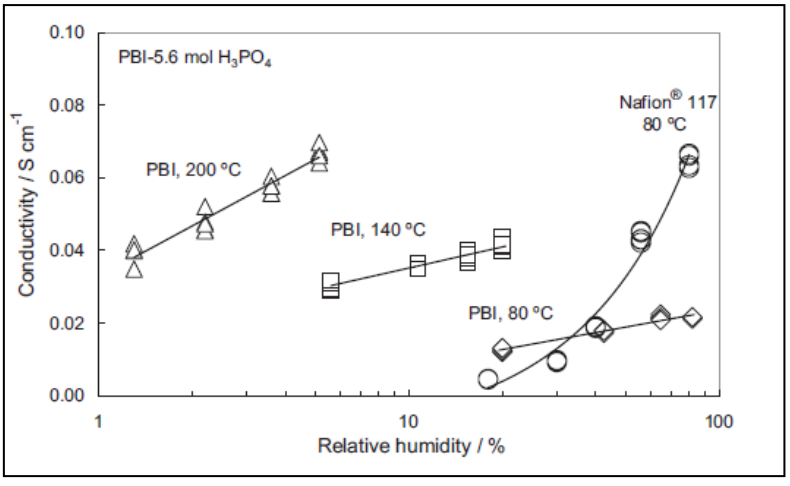


Figure (8): Variation of Conductivities of Nafion® and Phosphoric Acid Doped PBI Membranes with Relative Humidity at Various Temperatures (Li et al 2004).

Conclusion

This research paper aimed to measure the electrical conductivity of BSA doped PBI membranes in low and high operating temperature fuel cells. The main purpose of the electrical conductivity measurements is to compare the electrical conductivity performance of BSA doped PBI membrane performance against the electrical conductivity of PA doped PBI membrane at high operating temperatures and Nafion's membranes at low operating temperatures.

The 2-Pt probes technique was implemented to perform the electrical conductivity tests. 3 different concentrations 5, 6 and 7M of BSA solutions were prepared in order to be used to dope PBI membranes.

It was found that the relationship between the doping level and electrical conductivity of BSA doped PBI membranes was proportional at low operating temperatures (40 to 80^{o}C) whereas this effect was reversed at high operating temperatures.

On the other hand, the electrical conductivity of BSA doped PBI membranes exhibited poor performance in comparison of PA doped PBI membranes at high operating temperatures (100 to 180^{o}C) which was explained due to decomposition of the adsorbed BSA acid in the PBI membrane. Surprisingly BSA doped PBI membranes performed an outstanding behavior of electrical conductivity higher than Nafion's membranes at low operating temperatures (40-80^{o}C) which can be interpreted due to the presence of the sulfonated group on the acid structure.

More testing techniques on the BSA doped PBI membranes at low temperatures need to be carried out in order to investigate the oxygen reduction kinetics and fuel cell test polarization curves. These technical tests will help to compare BSA doped PBI membrane performance with Nafion's membrane at low operating temperatures. This would help to find a good alternative an organic acidic electrolyte to overcome the limitations for stated membranes in low and high operating fuel cells temperatures.

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