

دراسة بحثية لتقييم اداء الاحماض العضوية
كمحلول الكتروليتي لغرض تحسين
وتطوير تشغيل خلايا الطاقة كمعدات
منتجة للطاقة الكهربائية

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ملخص البحث بالعربية .

تعد اغشية خلايا الطاقة membranes المصنوعة من مركب بولي بنزايمزادول Polybenzimidazol والمعروفة بمركب البي بي أي PBI والتي تم تغطيسها و إشباعها بحمض الفوسفوريك H_3PO_4 أحد أهم الأغشية المستعملة في تركيب وتشغيل خلايا الطاقة المشغلة عند درجات حرارية عالية ترجع اهميتها بسبب قدرتها على التشغيل باداء عالي عند درجات حرارية عالية ، كذلك تمتاز بخاصية توصيل كهربائي عالية ، وميزة أخرى مهمة هي أنها تمتاز بتطارية منخفضة لحمض الكبريتيك عند درجات حرارية تصل الى اعلى من 150 درجة مئوية. من ناحية اخرى، توجد عدة عيوب لهذه الاغشية المشبعة بحمض الفوسفوريك والتي تتضمن خاصية امتصاص ضعيفة لغاز الاكسجين ، وايضا احد النقاط السلبية لها هو بقدرتها العالية على امتزاز ايونات الفوسفات السالبة على سطح البلاتين المستعمل كعامل محفز وتقليل ادائه وكذلك من عيوبها ايضا هو فقدان تسرب حمض الفوسفوريك من الغشاء عن طريق مخرج البخار و مجري الوقود الغازي. وعليه نتيجة لعيوب اداء اغشية البي بي أي المشبعة بحمض الفوسفوريك ، تهدف هذه الدراسة البحثية الى استكشاف ودراسة اداء بعض الاحماض العضوية لغرض ايجاد حمض الكتروليتي بديل لحمض الفوسفوريك عند درجات الحرارة العالية ذو اداء افضل من حمض الفوسفوريك لاغشية خلايا الطاقة. ثلاثة احماض عضوية تم اختيارها ودراسة ادائها وهي حمض خلاص الكلور Chloracetic acid ، وحمض البنزويك Benzoic Acid ، وحمض بنزين سيلفونيك Benzene sulfonic acid. الاختبارات العملية التي تم استعمالها لغرض دراسة الاحماض العضوية المذكورة سلفا هي اختبارات دراسة الموصلية الكهربائية للبروتونات proton conductivity ، كذلك اختبار قياس معدل تفاعل اختزال الاكسجين (ORR) oxygen reduction reaction وأيضا تم استخدام اختبار قياس منحنيات القطبية لخلية الطاقة fuel cell(I-V)

polarization curves. أظهرت النتائج المتحصل عليها من اختبارات الموصلية الكهربائية عند درجات حرارية عالية المدى بين 100 الى 180 درجة مئوية أن جميع الاحماض العضوية الثلاثة اظهرت اداء ضعيف للموصلية الكهربائية مقارنة بحمض الفوسفوريك. من ناحية اخرى ، عند درجات حرارية المنخفضة المدى بين (40-80 درجة مئوية) اظهر حمض بنزين سيلفونيك Benzene sulfonic acid افضل موصلية كهربائية بين الاحماض العضوية المذكورة ، وحتى موصليته كانت أعلى من حمض الفوسفوريك. هذه النتائج قد أدت بان يتم فقط اختيار ودراسة حمض benzene sulfonic ويتم تجاهل واهمال دراسة الحمضين العضويين الآخرين . في الخلاصة ، اختبارات CV و RDE و I-V كلها استنتجت واظهرت بأن حمض بنزين سيلفونيك Benzene sulfonic acid لم يكن بديل جيد ومناسب لحمض الفوسفوريك عند الدرجات الحرارية العالية وايضا لم يكن بديل مناسب لاغشية النافيون Nafion عند الدرجات الحرارية المنخفضة ويرجع سبب ذلك بانه عند الدرجات الحرارية العالية تحدث عملية جفاف والتكسير يسببها الحمض للغشاء ومن ناحية اخرى عند الدرجات الحرارية المنخفضة يسبب الحمض بتسمم سطح العامل المساعد وبالتالي تقليل ادائه.

A research study to assess organic acids performance as electrolytes to improve fuel cells operation as electrical energy devices.

Nomenclature

PEMFC: Polymer Electrolyte Membrane Fuel Cells

PEM: Polymer Electrolyte membrane

PBI: Polybenzimidazole

X: Doping level

PRU: Per repeated unit of PBI

TFMSA: Trifluoromethane sulfonic acid

PVPA: poly (vinylphosphonic acid)

MPPA: Monophenyl phosphoric acid

DPPA: diphenylphosphonic acid

(sPPA): sulfonated phenylphosphonic acid

DMAc: Dimethylacetamide

BA: Benzoic acid

CAA: Chloroacetic acid

BSA: Benzene sulfonic acid

PA: Phosphoric acid

SA: Sulfuric acid
R: resistance
 σ : conductivity
ORR: Oxygen reduction reactions
RDE: Rotating disk electrode
CV: Cyclic Voltammetry
LSV: Linear Sweep Voltammetry
AE: Auxillary electrode
RE: Reference electrode
WE: Working electrode
MEA: Membrane electrode assembly
 T_H : Humidifier temperature, °C
RH: Relative humidity, %

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFC) have been receiving a great amount of attention in the Automotive and stationary power sectors due to high power density and low operational temperature. In addition, they have been considered as alternatives for internal combustion engines for their high energy conversion, low CO₂ emissions and high efficiency [1], [2]

In the literature, one of the most traditional membranes that has been used for low temperature PEMFC is Nafion[®] (Du Pont Inc.). The presence of perfluorinated chain in Nafion membrane offers good chemical and mechanical stability below 90°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°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 [1]. The presence of poisonous species such as CO and H₂S in the fuel has a negative impact on the

performance of low temperature fuel cells due to catalyst deactivation [2]. For example, in Nafion based polymer membranes, the presence of CO content as low as 20 to 50 ppm in the gas feed stream will result in a significant decrease of fuel cell performance [3].

In order to overcome the above mentioned limitations for low temperature PEMFC, it has been suggested to increase the operation temperature of PEMFC [4-7]. The high temperature (HT) PEMFCs have 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 [8-10].

One of the most promising proton exchange membranes that operate at high temperature (more than 100°C) is Polybenzimidazol (PBI) doped with phosphoric acid. PBI has been used as fire resistant fabric for fire fighters clothes for its high thermal stability. Fig. 1 shows the chemical structure of PBI [11-12]

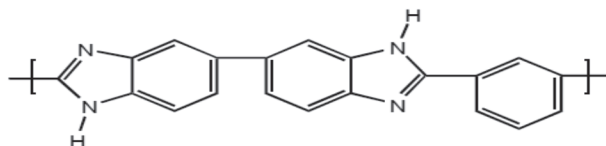


Fig. 1 Molecular structure of polybenzimidazol [12]

The ionic conductivity for PBI in the pure state is very low (10^{-12} S.cm⁻¹) [13-14]. An effective way to substantially increase the ionic conductivity of PBI is by doping it with different acids. Sulfuric acid, phosphoric acid, perchloric acid, nitric acid and hydrochloric acid have all been used to dope PBI [15]. Among the above acids is phosphoric acid has been considered to be the most promising acid due to its 3-D hydrogen bonding network, high thermal stability as well as high ionic conductivity at elevated temperatures and lower volatility at temperatures above 150°C [1].

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 electrocatalyst activity and strong adsorption of phosphate anions on the platinum catalyst surface combined with oxygen low solubility and sluggish oxygen reduction reactions [2].

Due to the aforementioned limitations of phosphoric acid as an electrolyte in doping PBI based PEMFC systems; the main target of this project research is to try to find an alternative organic acid as a doping electrolyte for PBI based high temperature PEMFC that could overcome those limitations. Three organic acids, chloroacetic, benzoic and benzene sulfonic acids, have been investigated in terms of proton conductivity, oxygen reduction kinetics and fuel cell I-V polarization curves. Phosphoric acid doped PBI membrane has been considered as a benchmark for this research study.

Methodology

Proposed Organic Acids Used to dope PBI Membranes:

Organic acids that have similar physical properties to phosphoric acid based on its boiling and melting points were considered. In other words, organic acids which have boiling points above 140 °C so that they could be used in high temperature fuel cells.

Three organic acids were selected for this project research as follows:

1. Chloroacetic acid.
2. Benzoic acid.
3. Benzene sulfonic acid.

These organic acids (chloroacetic, benzoic and benzene sulfonic acids) have been chosen as a dopant for polybenzimidazole (PBI). These three organic acids were compared with phosphoric acid in terms of proton

conductivity, oxygen reduction kinetics and I-V polarization curves for fuel cell test.

B. PBI Membrane Preparation

Firstly, the PBI-DMAc solution has been made as the following steps. PBI powder as shown in fig. 2 was supplied by [Between, Germany]. 12.5% weight percent of PBI in Dimethylacetamide (DMAc) solution was prepared. The PBI powder was mixed with DMAC in a PTFE vessel as shown in fig.3

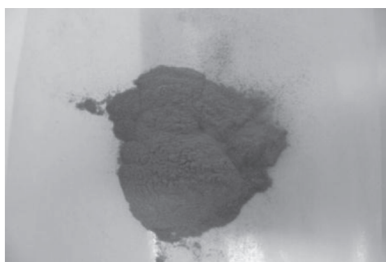


Fig. 2. Polybenzimidazole (PBI) powder

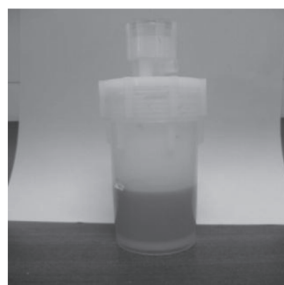


Fig. 3. 12.5% PBI-DMAc solution in a PTFE vessel

Afterwards, the 12.5% PBI-DMAc in a PTFE vessel was heated in a microwave oven with a power rating of 50W for 2 minutes. Then the PTFE vessel was taken out of the microwave, its lid subsequently opened to release the gas and then left to cool down for 5 min. During that time the PTFE vessel was shaken to mix the solution in order to dissolve the PBI particles.

Then the vessel was put in the microwave for just 1 minute. Afterwards, it was taken out again to release the gas and left for 5min before being shaken again.

The mentioned steps were then repeated about 9 to 10 times to make sure that almost all the PBI was dissolved in the DMAC solution.

The next step was to extract the undissolved PBI particles from the DMAc solution by putting it in a rotating centrifugal. Once the PBI-DMAc solution was purified, the next step was to make sure that the PBI weight percentage (%wt) in the DMAc solution is 12%. This was done by first weighing an empty petri dish (W_1), then by placing a small amount of the prepared PBI-DMAc solution on it and reweighing the petri dish (W_2). Once this was achieved, it was inserted into the air oven at a temperature of 80 °C for 30 minutes in order to evaporate the DMAc. Afterwards, the petri dish containing the PBI was weighed again (W_3).

The calculation to measure Wt% of PBI in DMAc solution was as follows:

$$W_1 = 24.0402 \text{ gm.}$$

$$W_2 = 24.6119 \text{ gm}$$

$$W_3 = 24.113$$

$$\text{Weight of (PBI+DMAc before drying), } W_4 = W_2 - W_1 = 24.6119 - 24.0402 = 0.5717 \text{ gm}$$

$$\text{Weight of PBI after drying, } W_5 = W_3 - W_1 = 24.113 - 24.0402 = 0.0729 \text{ gm}$$

% weight percentage of PBI in DMAc solution

$$= \frac{W_5}{W_4} \times 100 = \frac{0.0729}{0.5717} \times 100 = 12.75\%$$

C. Preparing Organic Acids Doped PBI Membranes

Chloroacetic acid (CA), $C_2H_3ClO_2$ (99.8%) was supplied by Sigma Aldrich. Three aqueous solution samples (4, 5 and 6M) were prepared and put in bottles of 20 ml size. In addition, a fourth pure sample of chloroacetic acid was prepared and put in the 20ml bottle.

Four PBI membranes of (1cm×2cm) and four PBI membranes of (3cm×3cm) for conductivity measurements and fuel cell test purposes respectively were cut from the original prepared 40 μm PBI membrane sheet. Before doping any PBI membranes with any organic acid solution, the (1cm×2cm) PBI

membranes had to be weighed and recorded as (W_1). In addition, the thickness of the above membranes was recorded. Afterwards, these PBI membranes were doped with an organic acid for a doping time of at least 7 days. In addition, the weight of the (1cm×2cm) PBI membrane after doping with an organic acid was recorded as W_2 .

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

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

The same procedure was done on the rest of the mentioned organic tested acids

D .Proton conductivity test measurement

A two Platinum (Pt) probe technique was used to measure the proton conductivity for the organic acid doped PBI membranes. The required apparatus for this technique included the Frequency Response Analysis (FRA) (Voltech TF2000, UK) that applied 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. The cell temperature was controlled by electronic thermocouple attached to both sides of the cell. One of the important factors of proton conductivity as was explained in chapter one was doping level, which is a ratio of moles of the acid doped in the PBI membrane to the repeated moles of PBI membrane [13]. Therefore, an initial indicator step for measuring proton conductivity was calculating doping levels of the organic acid in PBI membranes. For example, 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 =
 $0.0269(\text{gm})/308.336 (\text{gm.mol}^{-1}) = 8.72425 \times 10^{-5}$ moles

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

Therefore, doping level of 7M benzene sulfonic acid =
 $\frac{6.8 \times 10^{-4}}{8.72425 \times 10^{-5}} = 7.79$ per repeating unit (PRU)

Doping calculations for all organic acid doped PBI membranes were carried out in the same manner as that of the previous example of 7M of Benzene sulfonic acid doped PBI membrane except the direct casting of benzoic acid with PBI-DMAc solution. After calculating the doping level, the thickness of PBI membranes after doping with organic acids was measured in order to calculate the cross sectional area of the membranes. Afterwards, the doped PBI membranes was placed on two platinum (Pt) probes with spacing of 0.5cm of a cell test as shown in Fig. 4. Afterwards, the testing cell was closed and torqued. Once that was done, the testing cell was connected to the Ammeter, voltmeter and Frequency Response Analysis FRA . Then, the cell was heated between 80 and 200°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.

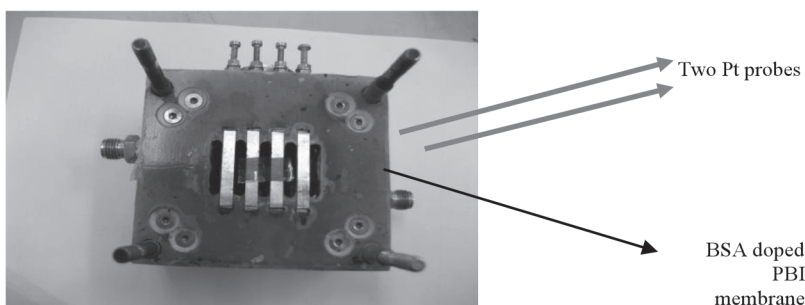


Fig. 4 (BSA) doped PBI membrane between two Pt probes.

The FRA was used to apply AC impedance frequency (from kHz to 20 kHz), then current and voltage readings were recorded using the voltmeter and ammeter in order to

calculate the electrical resistance (R) and proton conductivity (σ) at that temperature. Afterwards, the maximum value of the 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 for each acid and compared with the benchmark plot of phosphoric acid doped PBI.

E. Experimental section of half cell tests using CV and RDE techniques:

An electrochemical glass cell was set up with a reference electrode of (Ag/AgCl), a counter or auxiliary electrode of platinum, Pt wire and a working Pt rotating disk electrode [Radiometer Analytical, surface area = 0.07068cm^2]. After the three electrodes were placed in an electrolyte solution in the half cell they were connected to Auto Lab potentiostat PG state 302 and in order to record the voltage and current values when applying external voltages to the electrolyte.

Rotating Disk Electrode (RDE) measurements

Procedure

The kinetics measurements of oxygen reduction reactions for benzene sulfonic acid (BSA), sulfuric acid (SA) and phosphoric acid (PA) using CV and RDE techniques have been taken place under room temperature and atmospheric pressure conditions. The cell firstly was filled with an appropriate electrolyte to be tested. Then working, reference and counter electrodes were connected to the Auto lab PG 302 potentioostat properly. All reported voltages were relative to the (Ag/AgCl) reference electrode.

Afterwards, the cell was purged with oxygen for half an hour. The rotating disk electrode (WE) was dipped in the electrolyte. Then, the rotating disk electrode (RDE) was rotated at 1600 rpm. Meanwhile, the auto lab PG stat 302 potentiostat software was programmed as follows:

Conditioning potential: Open circuit voltage (OCV) + 40 mV
Duration time: 10 seconds

Equilibration time: 0

Number of scans: 1

Begin potential: OCV + 40 mV

End potential: 0.18V (vs. Ag/AgCl reference electrode)

Step potential: 0.0004V (1/100 of step scan rate).

Afterwards, the software was run. Once it had finished the cycle, the software was reprogrammed in the same fashion three more times and with the reproducibility of the curves being checked every time. Then the experiments were run at 400 rpm, 900 rpm, 1600 rpm and 2500 rpm and the aforementioned steps were repeated. Once this was achieved for each rotation speed the data was saved immediately.

F. Cyclic voltammetry measurements Procedure

Once all the RDE measurements were taken for an electrolyte solution, the cyclic voltammetry (CV) measurement steps for this electrolyte were started by firstly purging the electrolyte with Nitrogen for half an hour. Then RE, WE and AE were connected to the potentiostat. Afterwards, the auto lab potentiostat was programmed as follows:

Conditional potential: OCV

Start potential: 0.18V

First vertex potential: 1.1V

Second vertex potential: 0.18V

Scan rate: 0.02 V/sec

Step Potential: 0.0004V

Afterwards the scan was effectuated and once it was completed the data was saved.

G. Fuel Cells Test Preparations

Proton conductivity results for the tested organic acid PBI membranes revealed that their conductivity at high temperatures (100 – 200°C) were very low compared to H₃PO₄ PBI membranes. Therefore, a comparison in the performances between BSA doped PBI membranes and Nafion membranes at low temperatures (40 – 80°C) was carried out since BSA exhibited good conductivity at temperatures < 100°C.

IV. RESULTS AND DISCUSIONS

A. organic acids conductivity results

Fig.5 represents the experimental results of phosphoric acid doped PBI membrane conductivity, at high temperatures (80 – 100°C). It can be seen that the highest conductivity values were between 160 and 180°C around 0.04 S.com⁻¹. This conductivity value was in close agreement with the literature data [1].

However, as it has been mentioned in chapter one reference [1] that conductivity recorded values of H₃PO₄ doped PBI membrane vary considerably in the literature and depend on the membrane preparation method, pretreatment of PBI membranes, doping level of H₃PO₄ in the membrane, temperature and relative humidity .

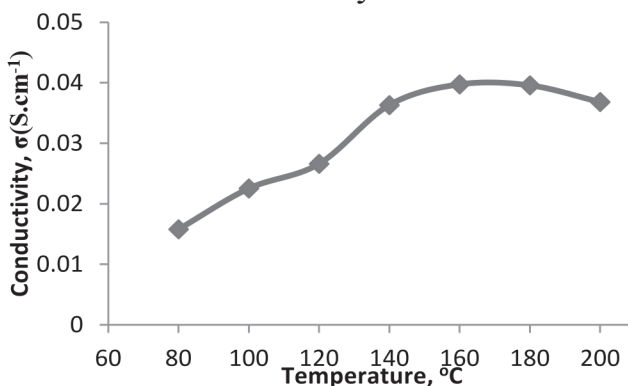


Fig. 5 PA doped PBI membrane conductivity between 80 and 200°C

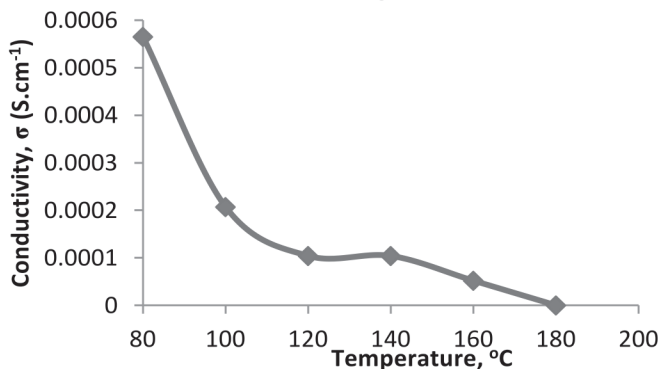


Fig. 6 conductivity of pure CAA doped membrane against temperature

Fig. 6 shows the proton conductivity of melted pure Chloroacetic acid doped PBI at a temperature range between 80 and 180°C. The reason why the conductivity data for 6 and 10 M CAA doped PBI membranes are not shown in the above figure is because their conductivity values in the above temperature range were negligible. In addition this figure shows that as the temperature rose, the conductivity of chloroacetic acid doped PBI membrane decreased substantially from $5.65 \times 10^{-4} \text{ S.cm}^{-1}$ at 80°C to lower than 10^{-6} at 180°C. It was noticed that the highest conductivity for this acid doped membrane was demonstrated by the pure melted sample of chloroacetic acid i.e. 99.8% purity. In contrast, Robert et al [15] found that the trichloroacetic acid conductivity increases in more diluted solution i.e. lower electrical resistivity ; 1240 and 23 $\Omega \text{ cm}$ at 25°C for the 90% and 70% weight percent of trichloroacetic acid, respectively.

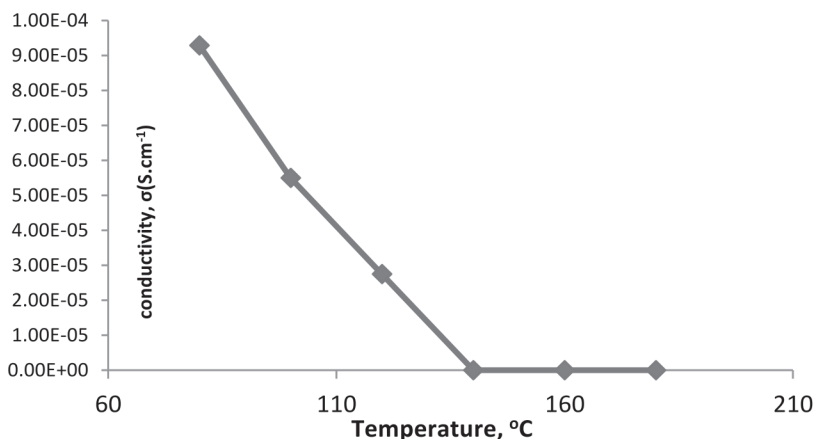


Fig. 7 BA doped PBI membrane conductivity variation against temperature

Fig. 7 shows the conductivity of benzoic acid as a function of the temperature. This figure reveals that benzoic acid doped PBI conductivity is significantly lower than that of chloroacetic acid. For instance, at 100°C, the proton conductivity of melted chloroacetic acid PBI membrane was $2.07 \times 10^{-4} \text{ S.cm}^{-1}$.

Meanwhile, it was $5.5 \times 10^{-5} \text{ S.cm}^{-1}$ for benzoic acid doped PBI

at the same temperature. However, the very low conductivity of benzoic acid doped PBI was expected. Robert et al [15] found that the conductivity of benzoic acid solution had the worst conductivity (highest resistivity) among six tested organic acid solutions about 2.1×10^7 and $1.9 \times 10^7 \Omega \text{ cm}$ at 135 and 153°C respectively. In addition, this acid has a very low solubility in water.

Fig.8 shows the proton conductivity of various doping levels of benzene sulfonic acid doped PBI membranes as a function of temperature. This figure shows undesirable behavior of proton conductivity of BSA doped PBI membranes. BSA doped PBI experienced lower proton conductivity at higher temperatures in the range between 100 and 180°C. In addition, a surprising fact was revealed from this figure, namely the fact that the conductivity of this acid doped PBI membrane decreased as the doping level was raised. The reason behind the above detrimental performance of BSA doped PBI conductivity at high temperature could be due to undergoing decomposition of the BSA since it was noticed that the BSA PBI membrane color changed from reddish brown before testing to blackish brown after testing. This behavior was recorded by Robert et al [15] in which 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. In comparison, BSA doped PBI membrane conductivity test took place in the presence of two Pt-probes. However, the decrease in conductivity as the doping level was raised might be due to the lack of water content in the membrane

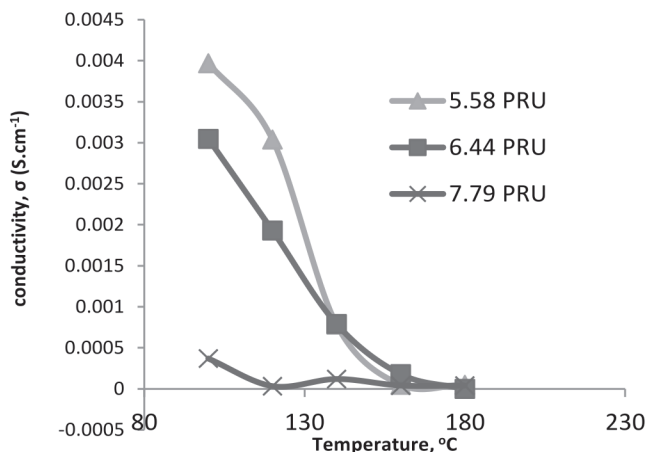


Fig. 8 Conductivity of BSA doped PBI membranes with high temperatures (100 – 180°C) at various doping levels.

However, in a comparison of the proton conductivity of BSA doped PBI membranes with CAA and BA doped PBI membranes conductivity as shown in fig. 9. It can be seen that at high temperatures (100 - up to 160°C), BSA doped PBI membranes showed higher proton conductivity than CAA and BA doped PBI membranes, as this was around 19 and 70 times greater in magnitude respectively at 100°C. Therefore, BSA doped PBI membrane was selected to be compared with phosphoric acid doped PBI membrane conductivity performance.

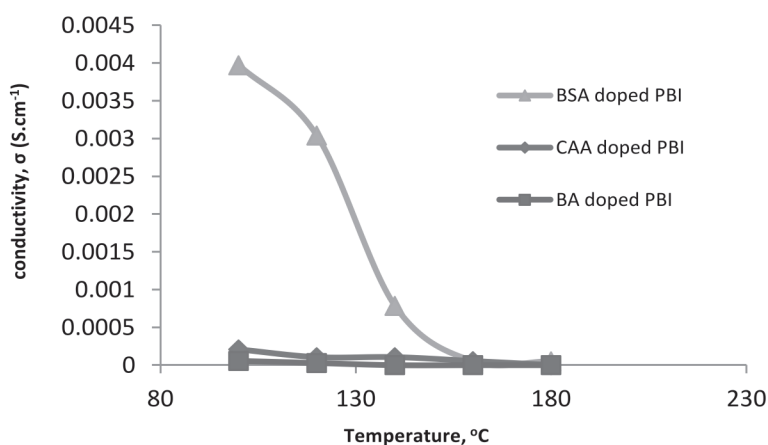


Fig. 9 a comparison of organic acid doped PBI membranes conductivity, BSA, CAA doped PBI and BA doped PBI

Fig. 10 compares the conductivity performance for phosphoric and benzene sulfonic acids doped PBI membranes at high temperature in the range between (100 – 180°C). In addition, this figure reveals that the conductivity performance of PA doped PBI membranes were greater than that of BSA doped PBI membranes. Therefore it can be concluded that BSA doped PBI membranes are not comparable and not suitable alternatives for PA doped PBI membranes at high temperatures (100 – 200°C). Due to the weak performance of BSA doped membranes at high temperatures, it was suggested to investigate the conductivity behavior of BSA doped PBI membranes at low temperatures in the range of (40 – 80C).

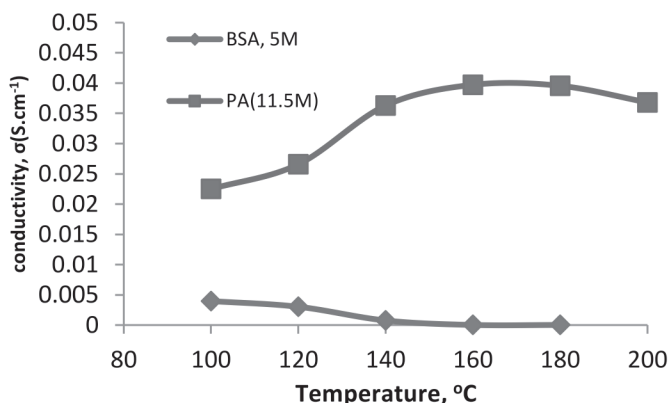


Fig. 10 Conductivity comparison of PSA and PA at high temperatures

Fig. 11 reveals that the conductivity of BSA doped PBI membranes was significantly higher at low temperatures in the range of (40 – 80°C) than high temperatures (100 – 180°C), particularly at 40°C about 0.28379 S.cm⁻¹. This value was even higher than the conductivity of Nafion hydrated membranes (0.094, 0.089 and 0.059 S.cm⁻¹) with thicknesses of 210×10⁻⁴, 110×10⁻⁴ and 60×10⁻⁴ cm, respectively at 80°C [16]. In

addition, fig. 14 shows that at 70°C the conductivity of BSA doped PBI (7.79PRU) is almost 0.1 S.cm⁻¹ which is higher than the conductivity of the commercial Nafion NRE 211 about (0.05681 S.cm⁻¹) [17] and Nafion[®] 117 around 0.068 S.cm⁻¹ [18]. In comparison with H₃PO₄ doped PBI membranes, conductivity of BSA doped PBI membrane at 70°C is 0.1 S.cm⁻¹ which has been greater than the conductivity of H₃PO₄ doped PBI membranes (0.038 S.cm⁻¹ at 140°C).

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. However, as the temperature rises above 100°C, the conductivity drops. This behavior has caused concerns about the expected incoming results for oxygen reduction reaction (ORR) kinetics and fuel cell polarization curves. Therefore, it was suggested to compare the performance of BSA doped PBI with Nafion 112 at low temperatures in terms of oxygen reduction reaction, ORR kinetics and fuel cells polarization curves.

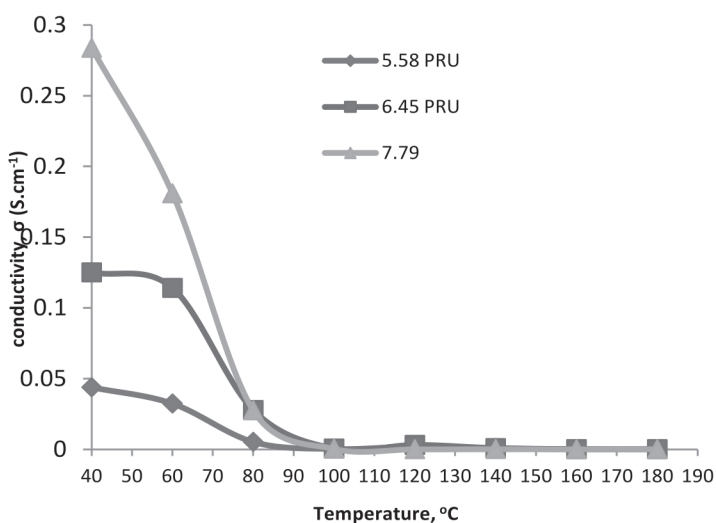


Fig. 11 BSA doped PBI membranes conductivity variation with doping levels at low and high temperatures.

B. Rotating Disk Electrode (RDE) measurement results

Fig. 12 compares the oxygen reduction reactions (ORR) kinetics for PA, SA and BSA solutions using a Pt rotating disk electrode. At low current densities, weak oxygen reduction reaction kinetics was observed which could be due to fairly high overvoltage losses which are about 220mV [19]. It can be seen that H₂SO₄ supports higher current densities and had the highest limiting current about 4×10^{-4} A. For instance, at overpotential of 0.2 V, the current densities of BSA, H₃PO₄ and H₂SO₄ were approximately 2.5×10^{-5} , 2.49×10^{-4} and 3.25×10^{-4} A/cm² respectively. However, BSA had the lowest limiting current around 1×10^{-4} A. In addition, at low exchange current densities, BSA suffered higher activation polarization compared to the other acids due to very slow oxygen reduction reaction kinetics on the Pt catalyst surface that could be as a result of very high adsorption of its anions on the platinum surface causing a poisoning effect of the Pt catalyst [20].

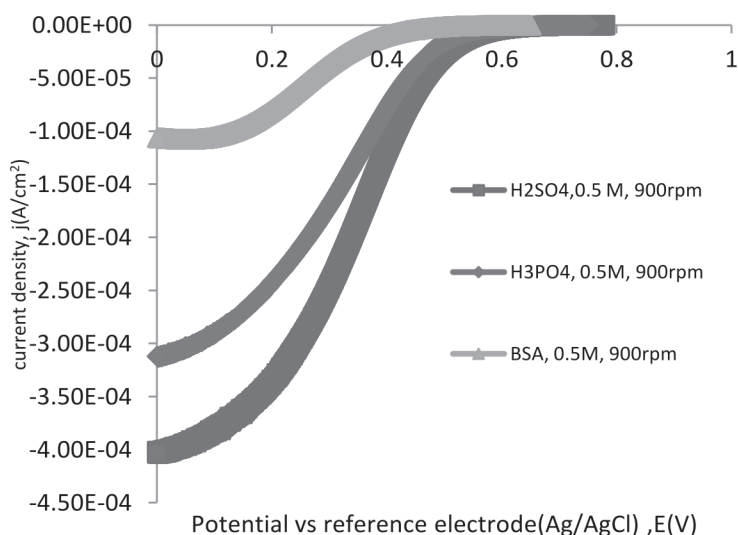


Fig. 12 linear sweep voltammetry measurements of (PA), (SA) and (BSA) solutions with rotating speed of 900 rpm.

C. Cyclic voltammetry (CV) measurements results

Fig.13 compares cyclic voltammetry graphs for PA, SA and BSA acids solutions at scan rate of 100 mV/s. It can be seen that the CVs for H_3PO_4 and H_2SO_4 acids solutions gave clear hydrogen, double layer and oxygen regions. These clear and identified regions are a sign of high purity of these electrolytes [21]. However, the hydrogen adsorption and desorption current peaks were not well defined in BSA cyclic voltammetry graph. In addition, it can be noticed that increasing scan rate resulted in worse hydrogen/oxygen regions. In addition, Fig. 13 reveals that the potential of the oxygen reduction reaction (ORR) kinetics of BSA is very poor compared to H_3PO_4 and H_2SO_4 acid solutions.

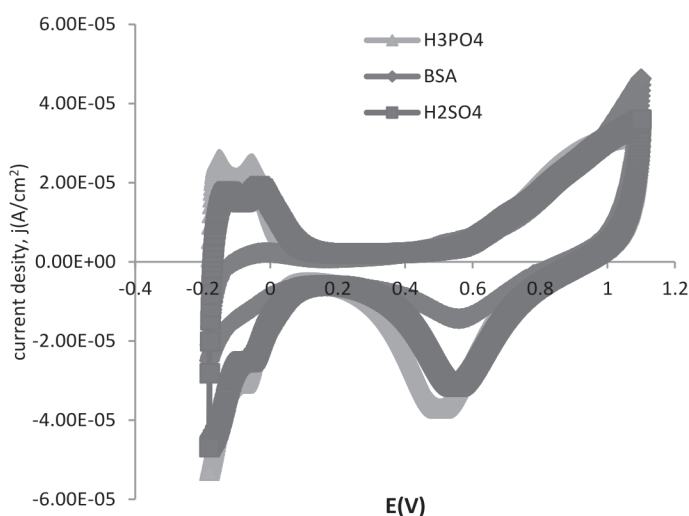


Fig. 13 a comparison of steady-state cyclic voltammetry of 0.5 M of BSA, PA and SA solution at room temperate and scan rate of 100 mvs

D. Fuel cells I-V polarization curves results

Fig. 14 compares the polarization curves of BSA doped PBI membrane with Nafion 112 membrane at 20°C in H_2/O_2 low temperature fuel cell. The literature data [22] of polarization curves of Nafion membranes 112 at 23°C and 3atm was quite consistent with the above experimental results of Nafion 112

which took place at 20°C and atmospheric pressure. It can be noticed that for the literature data, the open circuit voltage (OCV) about 0.94 mV was higher than the experimental data voltage for Nafion 112 cycle 20 about 0.85 mV. This difference can be due to the fact that at higher operation pressure, the overall voltage cell performance improves higher than at lower operation pressures [22]. It can be clearly seen that the performance of Nafion 112 is significantly higher than BSA doped PBI membrane. The evidence of the presence of acid anion poisoning effects on the BSA I-V polarization curve was that the open circuit voltage (OCV) of cycle 20 decreased by almost 300 mV compared to cycle one resulting in high overpotential losses. Meanwhile, the performance of Nafion 112 membrane at cycle 20 improved by almost 100 mV compared to cycle one. Therefore, due to the poisoning effect of BSA on the Pt catalyst, the fuel cell polarization test experiment was not measured at higher temperatures such as 30, 40, 60 and 80°C. Therefore, it can be concluded that benzene sulfonic acid doped PBI membrane is neither a suitable alternative for phosphoric acid doped PBI membranes at high temperatures nor for Nafion membranes at low temperatures due to the hydrolysis and decomposition effects at high operation temperatures and poisoning effects due to high acid anion adsorption at low temperatures.

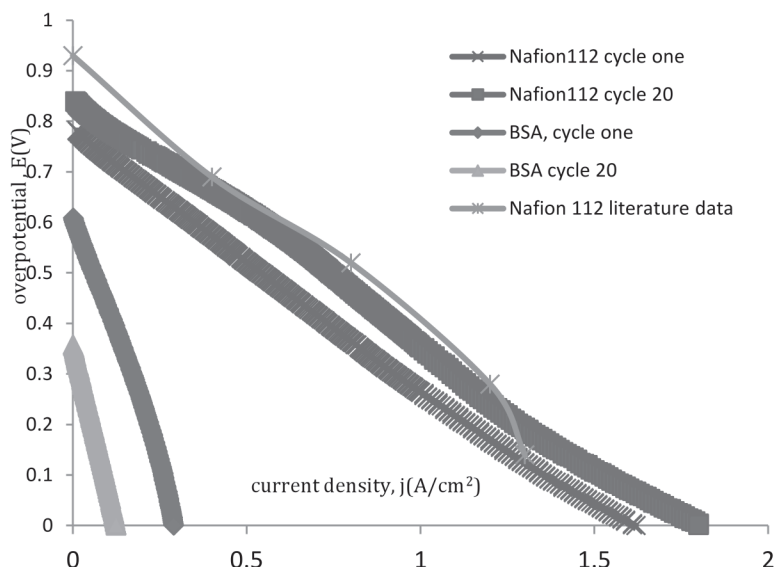


Fig. 14 a comparison of oxygen reduction polarization curves between Nafion membrane and BSA doped PBI membrane in H_2/O_2 low temperature fuel cell at $20^\circ C$, $T_H = 30^\circ C$

V. Conclusion

This research paper has aimed to study the potential of three selected organic acids to be a suitable organic acid alternative to phosphoric acid as a dopant for PBI membranes. These three organic acids (chloroacetic acid, $C_2H_3ClO_2$, benzoic acid, $C_7H_6O_2$ and benzene sulfonic acid, $C_6H_6O_3S$) have been investigated.

It was found that benzene sulfonic acid BSA (5.58PRU) doped PBI membranes had the highest conductivity about $(3.97 \times 10^{-3} \text{ S.cm}^{-1})$ at $100^\circ C$) compared to chloroacetic acid (5.8PRU) doped PBI membrane at around $2.07 \times 10^{-4} \text{ S.cm}^{-1}$ and benzoic acid (3.75PRU) doped PBI membrane at approximately $5.5 \times 10^{-5} \text{ S.cm}^{-1}$ at the same conditions. However, compared to the conductivity of phosphoric acid doped PBI membrane (0.0225 S.cm^{-1}) at $100^\circ C$ the above conductivity of benzene sulfonic acid doped PBI membrane was significantly lower. Therefore, it was concluded that all the above organic acids

doped PBI membranes were not a suitable alternative to H_3PO_4 doped PBI membrane at high temperature fuel cells.

The strategy of this study has been shifted to study the conductivity of these acids at low temperatures in the range of 40 – 80°C. Then, it was found that the conductivity of benzene sulfonic acid doped PBI membranes at 70°C was 0.1 S.cm⁻¹ with doping level of (7.79 PRU). This conductivity results has been considerably greater than the conductivity of H_3PO_4 doped PBI membranes at 140°C which was 0.038 S.cm⁻¹ and the conductivity of Nafion NRE 211 about (0.05681 S.cm⁻¹). Therefore, it was decided to study the potential of benzene sulfonic acid doped PBI membranes at low temperatures and to compare it with Nafion 112 membranes at low temperatures. The comparison study between benzene sulfonic acid doped PBI membranes and Nafion 112 membranes at low temperatures was based on the study of oxygen reduction reaction (ORR) kinetics of using cyclic voltammetry and rotating disk electrode techniques considering phosphoric and sulfuric acid solutions as benchmarks for this test and steady-state polarization (I-V) curves. The rotating disk electrode results revealed that 0.5 M of benzene sulfonic acid solution had the lowest limiting current around 1×10^{-4} A/cm² comparing to 3×10^{-4} and 4×10^{-4} A/cm² limiting currents of 0.5 M of phosphoric and sulfuric acids solutions, respectively. In addition, at low current densities, benzene sulfonic acid exhibited the least favourable oxygen reduction reaction kinetics compared to the other two acids. On the other hand, steady-state cyclic voltammetry data for benzene sulfonic acid solution showed unclear hydrogen and oxygen regions in contrast to phosphoric and sulfuric acid solutions which their regions were significantly identified. The hydrogen adsorption and desorption peak currents of benzene sulfonic acid solution was dramatically lower than those for phosphoric and sulfuric acid solutions. Therefore, the CV and RDE tests concluded that the poor oxygen reduction reaction kinetics performance of

benzene sulfonic acid tests could be due to high adsorption of acid anions on the Pt catalyst surface causing a poisoning effect on the catalyst electrode.

On the other hand, the polarization (I-V) curves revealed that the performance of Nafion 112 membranes was significantly higher than that of benzene sulfonic acid doped PBI membranes at 20°C and ambient pressure. Since those curves showed that the open circuit voltage (OCV) of BSA doped PBI membranes of cycle 20 decreased by almost 300 mV compared to cycle one resulting in high overpotential losses. This behaviour was proof of the poisoning effect for benzene sulfonic acid anions on the catalyst surface. In contrast, the performance of Nafion 112 membrane at cycle 20 improved by almost 100 mV compared to cycle one.

Overall, it has been concluded that benzene sulfonic acid doped PBI membrane was neither a suitable alternative for phosphoric acid doped PBI membranes at high temperatures nor an alternative to Nafion membranes at low temperatures due to the hydrolysis and decomposition effects at high operation temperatures and poisoning effects due to high acid anion adsorption at low temperatures.

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