ePProceedings Chemistry 5 (2020) 21-25

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

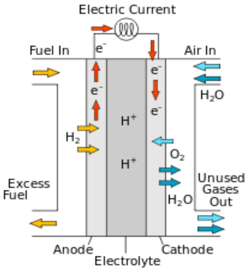
Fabrication of Polybenzimidazole Membrane Based on Phosphotungstic Acid Doped For Fuel Cell Application

Nur Fatin Atiqah Mohd Faudzi and Hadi Nur*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
**Corresponding Author:* hadinur@utm.my

Article history:
Received 1 Sept 2020
Accepted 30 Sept 2020

GRAPHICAL ABSTRACT



Schematic diagram of fuel cell

ABSTRACT

In this study, phosphotungstic acid (PWA) doped polybenzimidazole (PBI) membranes were prepared by solution casting method with different content of PWA (0.05 M, 0.10 M and 0.15 M) for proton exchange membrane fuel cell (PEMFC). PWA was used for improving the properties of high temperature PBI based proton exchange membranes. The effect of inorganic filler on the membrane structural and optical absorption properties were investigated by using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR spectroscopy) and diffuse reflectance ultraviolet visible-spectroscopy (DR-UV Vis spectroscopy). Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) micrograph reveals the dispersion of PWA in the PBI matrices. Electrochemical impedance spectroscopy (EIS) was used to evaluate the proton conductivities of the membranes. The best results are observed when the membrane with composition 25wt% of PBI are doped with 0.15 M PWA gave proton conductivity of 2.32 x 10^{-11} S/cm which is higher than pristine PBI membrane. The incorporation of PWA in the PBI-based membranes showed improved proton conductivity. It was also found that the fuel cell performance can be improved by optimizing the weight percent of the PBI polymers and content of the acid. Thus, the addition of inorganic heteropolyacid (HPA) into PBI significantly increase the proton conductivity of PBI membranes and can be better candidates for fuel cell application.

Keywords: Fuel cell, polybenzimidazole, phosphotungstic acid, proton exchange membrane fuel cell, proton conductivity

1. INTRODUCTION

For the past thousands of years, peoples have relied more on the world supply of burning fossil fuels to generate energy. As the world population had increase, as a result more demands on energy consumption and the cost of using them has also increased. Due to its high level of pollution, the depletion of fossil fuels based energy resources on that time is widely explored. Among the different alternative sources of energy, fuel cells are the most reliable choice which continually transforms the chemical energy into electrical energy in an electrode-electrolyte system [1]. Proton exchange membrane fuel cells (PEMFCs) have the advantage of being efficient sources of energy production with desirable technology for energy conversion, low operating temperature, high efficiency, zero emissions, short start-up time and silent service [2]. Polybenzimidazole (PBI) was found to be the most promising candidate for fuel cell due to its high thermochemical resistant, low cost and high conductivity at higher temperature under anhydrous conditions for electrolyte membrane. However, owing to the lack of conduction media for proton transportation, the pristine PBI membrane has poor ionic conductivity. High proton conduction mechanism within the membrane can only manage with required amount of acid doping level (ADL) [3].

The incorporation of heteropolyacids (HPAs) such as phosphotungstic acid (PWA) represent a type of inorganic fillers was addressed by several studies as a new proton conducting materials. In this research, the main focus is to investigate on how the acid doped-PBI-based membrane will impact on proton conductivity.

2. EXPERIMENTAL

The experiment was divided into two main stages. The first stage was focused on the preparation of the PBI polymers solution. The membrane casting solution were prepared in a fume hood by dissolving PBI powders with different weight composition (15wt% and 25wt%) in N, N-dimethylacetamide (DMAc) solution with the aid of lithium chloride followed by reflux on a hot plate with a stirrer connected with glass condenser at 130°C for 24 hours in the paraffin oil. The resulting viscous solution is decanted onto a glass plate and casting at room temperature. The glass plate was further treated in an oven at 80°C for 24 hours. The membranes obtained was further treated in a water bath at 80°C for an hour to remove residual solvent before dried in oven at 110°C for another 24 hours.

The second stage was focused on the acid doping on PBI membrane. After forming the membrane, acid doped membranes were prepared by dissolving the membrane in phosphotungstic acid solutions with different concentration (0.05M, 0.10M and 0.15M) for 24 hours at room temperature. The acid-doped membranes were dried in oven for at 110°C for 24 hours. The weight gain before (W_0) and after doping (W_1) was recorded by measuring the mass obtained by the membrane. The PWA_{dop} will be calculated according to the following equation:

$$\mathrm{PWA_{dop}} = \frac{[(W_1 - W_0)/Mw_{(PWA)}]}{[W_0/Mw_{(PBI\ repeatunit)}]}$$

in which M_W (PWA) and M_W (PBI repeat unit) are the molecular weights of PWA (g/mol) and PBI repeat unit (g/mol), respectively.

3. RESULTS AND DISCUSSION

3.1 Surface chemical analysis of PBI-based membranes

ATR-FTIR was used to determine the chemical structure of the PBI-based membranes. Figure 1 shows the spectra of 15wt% of PBI and 25wt% of PBI membranes. The absorption at 3120 cm^{-1} was attributed to the free N-H stretching vibrations of the benzimidazole ring. The peaks at 1630 and 1440 cm^{-1} shows the characteristic of the benzimidazole ring and these bands were assigned to the C=N and C=C stretching vibration bands respectively. The absorption peaks in range 2500-2250 cm^{-1} is relatively low intensity and might correspond to the in-plane C–H deformation. The peaks at 1530 cm^{-1} was attributed to the characteristic's absorption of the benzene rings.

For PBI/PWA membrane, the presence of PWA molecules contain a cage of tungsten atoms linked by oxygen atoms with tetrahedral phosphate group. The presence of PWA molecules can be recognized by the presence of the finger-print bands below 1100 cm^{-1} which correspond to the oxygen atoms bonds which is 1081 cm^{-1} (P-O), 967 cm^{-1} (W=O) and 804 cm^{-1} (W-O-W) [4]. As can be seen in Figure 1 (a-b), the major peaks for the Keggin structure of the PWA clusters does not show apparent characteristic peaks in the PBI/PWA membranes which probably due to the overlapping with other peaks in the fingerprint region. However, the success of the phosphonation step in the structure of PBI-based membranes is thus confirmed by a very broad absorption of O-H band between 3500-2500 cm^{-1} with lower intensity in comparison of pristine PBI membrane. These broad absorptions is due to the strong interactions between phosphonic acid and imidazole rings through hydrogen bonding [1].

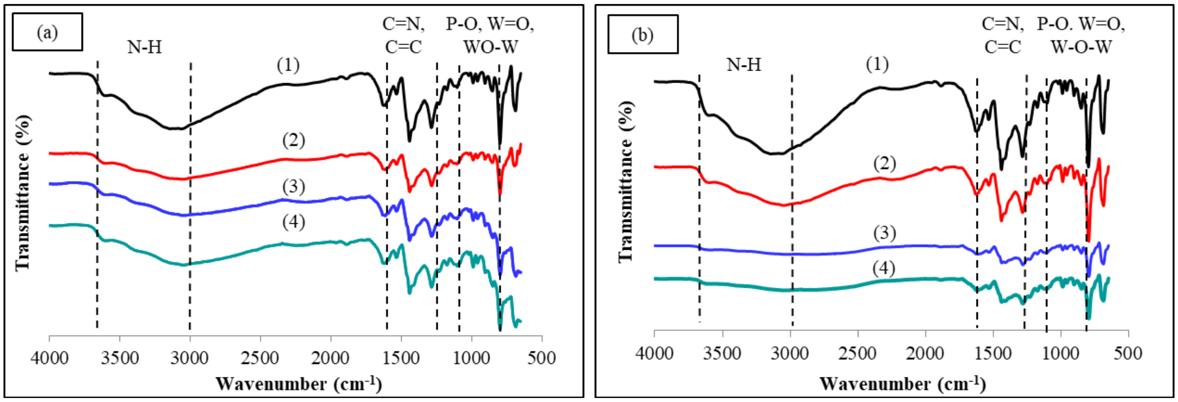


Figure 1. FT-IR spectra of PBI (a) 15wt% (b) 25wt% (1) pristine PBI, (2) PBI/PWA 0.05M, (3) PBI/PWA 0.10M and and (4) PBI/PWA 0.15M.

3.2 SEM measurement of PBI-based Membranes

The morphologies and cross-section of pristine PBI and the PBI/PWA membranes were characterized by using SEM with 1000x and 5000x magnifications. Figure 2(a-1) shows the surface morphologies of the pristine PBI membrane showed a homogeneous surface with no agglomerates and exhibit pore free structure which would appear as black spots in SEM images [5]. Figure 2(a-2) shows the cross-section of the pristine PBI membrane was smooth without phase separation or through holes, indicating the fine quality of the membrane. After doping with PWA, the white spots are observed on the surface of doped membrane represent the PWA clusters inside PBI-based membrane as shown in Figure 2(b-1). The white spot became more and intensive as the concentration of PWA increase [6]. The cross-sectional of the doped membrane showed the formation of channels due to the presence of the PWA clusters and this reflected in the appearance of holes indicated the strong interaction of PWA with the PBI matrix as shown in Figure 2(b-2). The homogeneous mixture of PWA clusters in the PBI matrix promotes higher transportation of water molecules through the development of new path channels. This SEM images presented additional proof of miscibility between PWA and PBI by hydrogen bonding [7].

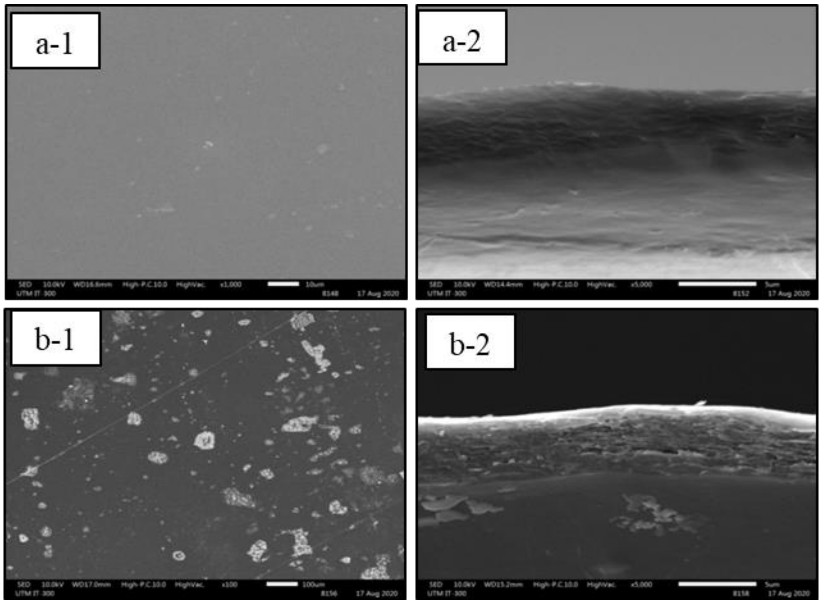


Figure 2. SEM images of 25wt% PBI (a) surface morphology (b) cross-section morphology of (1) pristine PBI (2) PBI/PWA 0.15M

3.3 Optical properties of PBI-based membranes

DR/UV-Vis is one of the methods to study the molecular interaction among PBI molecules in the membrane [8]. Figure 3(a) and (b) shows the DR UV-Vis spectra of different (wt%) of PBI and acid content. There are two peaks appear in both DR-UV-Vis spectra which is located around 270 nm and 370 nm. These two peak were assigned to the n-π* and π-π* transitions respectively. A decreasing in intensity indicate the existence of the π-π interactions in the aromatics rings in PBI and this interaction leading to an ordered structure which caused the arrangement of aromatics ring are closely stacked together. This reducing intensity is called quenching phenomenon. However, when PWA was added into the PBI-based membrane, the intensity of acid doped membrane shows is higher than the pristine PBI. This is because the presence of PWA molecules caused the original hydrogen bonding in PBI become loose as PWA molecules have a strong tendency to form hydrogen bonding with PBI groups.

Their interaction leads to the breaking up of molecule stacking of the polymeric structure of PBI and show up in electronic transitions as shifts in wavelength as well as intensity changes [8]. Overall, these results shown are in a good agreement to the morphological properties studies.

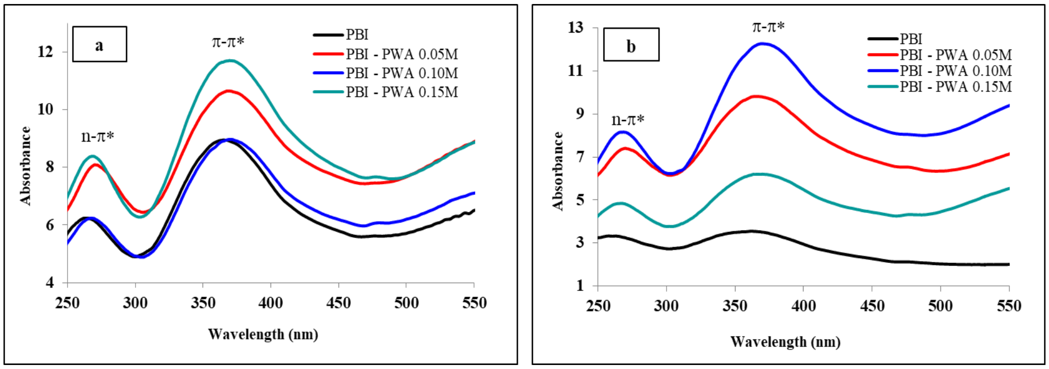


Figure 3. DR-UV Vis spectra of PBI (a) 15wt% (b) 25wt%

3.4 Proton conductivity measurement of PBI-based membranes

Electrochemical impedance spectroscopy (EIS) was used to evaluate the proton conductivities of the membranes. All the samples were prepared in the same dimensional area of 4 cm^2 for an effective comparison. However, the thickness of the membrane was hard to be controlled due to different usage of glass plate for solution casting method. Accordingly, the higher acid doping level provides more number of acid sites hence increase the conductivity of the membrane. As expected, the proton conductivity values of the PBI-based membranes showed increased pattern with an increasing quantity of acid doped as shown in Table 1. The results showed proton conductivity of the doped membranes with an optimal PBI composition of 25wt% doping with 0.15 M PWA giving the highest proton conductivity of 2.32 x 10^{-11} S/cm.

It was seen that the introduction of PWA as acidic filler into PBI membrane enhanced the proton conductivity. The enhanced conductivity was described in the Grotthuss proton hopping and vehicle mechanism. The PWA clusters in the prepared membranes provides H_3O^+ as charge carrier ion and interact with imidazole ring in the PBI backbone allowing proton to jump along molecular chain and facilitate proton transport through hydrogen bond formation creating a new conduction pathway for proton transfer [9]. It can be concluded the presence of PWA clusters provide more reachable route for proton transfer through the membrane, thereby improving the PBI-based membrane proton conductivity.

Table 1. Proton conductivity measurement of PBI-based membranes

Samples	**Average thickness (cm 10^{-3})**	**|Z| (ohm)**	**Area (cm^2)**	**σ ($S\ cm^{-1}$)**
15wt.% pristine PBI	1.3	4.58 x 10^8	4	7.09 x 10^{-13}
15wt.% PBI/PWA-0.05M	1.3	2.03 x 10^8	4	1.61 x 10^{-12}
15wt.% PBI/PWA-0.10M	1.4	1.33 x 10^8	4	2.65 x 10^{-12}
15wt.% PBI/PWA-0.15M	1.6	6.70 x 10^7	4	5.97 x 10^{-12}
25wt.% pristine PBI	2.5	2.95 x 10^8	4	2.13 x 10^{-12}
25wt.% PBI/ PWA-0.05M	2.4	1.33 x 10^8	4	4.54 x 10^{-12}
25wt.% PBI/ PWA-0.10M	2.7	9.43 x 10^7	4	7.18 x 10^{-12}
25wt.% PBI/ PWA-0.15M	2.6	2.86 x 10^7	4	2.32 x 10^{-11}

4. CONCLUSION

As a conclusion, this research has successfully achieved all of the objectives. Polybenzimidazole membranes containing different content of PBI and PWA concentration were prepared by solution casting method. Pristine PBI and PWA doped PBI membranes were structurally and morphologically characterized by ATR-FTIR, SEM, DR-UV Vis and EIS. The FT-IR and DR-UV-Vis results indicated a chemical interaction occurred between PBI and PWA. The use of phosphotungstic acid was reflected in the formation of channels in the polymeric network as observed by cross-section SEM images. The optimization of polymer concentration and acid concentration parameter was successfully done. The results showed proton conductivity of the doped membranes with an optimal composition of 25wt% PBI doping with 0.15 M PWA giving the highest proton conductivity of 2.32 x 10^{-11} S/cm compared to pristine PBI and other doped membranes. Thus, the incorporation of phosphotungstic acid into polymer matrix has a major impact on PBI based membrane efficiency. These results showed doped membranes can become a potential membrane for polymer electrolyte membrane fuel cell because of its high conductivity fuel cell performance.

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