Evaluation of H_3PO_4 doped PBI-I membrane as H_2/O_2 Fuel Cell

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Abstract: *PBI-I was synthesized by condensing 3,3'- diaminobenzidine (DAB) and Isophthalic acid(IPA) by solution polycondensation method using polyphosphoric acid (PPA). PBI-I has inherent viscosity ≥1dl/gm. Four dense membranes with different thickness were prepared by solution casting method under identical conditions using 3%(w/v) polymer solution in Dimethylacetamide (DMAc). Membranes samples of 4x4cm^2 with different thickness were dipped in H_3PO_4 solution of various concentrations. The dip time required to achieve maximum possible doping was initially determined by keeping the PBI-I membranes in H_3PO_4 (16.2M), followed by vacuum drying at 100°C for three days. Doped membranes samples were prepared with different doping level and their performances were tested. Among the four doped membranes, membrane with thickness 91.6micron and doping level 10.88mol/ RU gave better performance, having the OCV value 0.9V, current density1.76A/cm^2 and power density 450mw/cm^2 at 175°C. These membranes can be used as proton conducting membrane for Fuel cell application.*
Keywords: *Polybenzimidazole(PBI), Phosphoric acid doped membrane, Fuel cell performance evaluation*

I.   Introduction

Polybenzimidazole (PBI) is heteroaromatic polymers known from the early work on fuel cell [1]. PBI synthesized from 3,3- diaminobenzidine and isophthalic acid is gaining increasing importance as the proton exchange membrane (PEM) material remarkable thermal stability, mechanical property, chemical resistance, fiber forming property, adhesion property, etc[1-3]. Fuel cell based on its membrane can be operated up to 200°C [2,3]. Polybenzimidazole have high CO tolerance [2,3], low fuel crossover [3,4], almost zero osmotic drag coefficient [4] and proton conductivity comparable to Nafion membrane [2–4]. The high basicity of material is characterized by high density [5,6], high Tg [6], H_3PO_4 uptake of ~14 moles per repeat unit (mol/RU) and 3.4–3.6 mol/RU of water sorption [7]. Applications of PBI in fiber and fabrics [8], as a membrane material [9–12], structural adhesives [13], hydrogen sensor [14], blends [15,16], composites with other polymers for various applications like microcellular foam [17], as a catalyst support in epoxidation of alkenes [18], nanofiber [19], etc. are documented. Owing to high thermal stability [20,21,26], PBI finds application in aerospace industry also [22]. One of its important drawbacks includes limited solvent solubility [23,24]. It is soluble only in N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethylsulphoxide (DMSO) and N-methylpyrrolidinone (NMP) [25]. In the present work, we are reporting application of H_3PO_4 doped PBI-I membranes with different thickness and doping levels as proton exchange membranes for construction of H_2-O_2 fuel cell.

II.   Experimental

2.1 *Polymer Synthesis:*

The PBI was synthesized by condensing 3,3'- diaminobenzidine (DAB) and isophthalic acid (IPA, AR Grade) in polyphosphoric acid(PPA) as a solvent at 200°C for 20 h as per Scheme1.
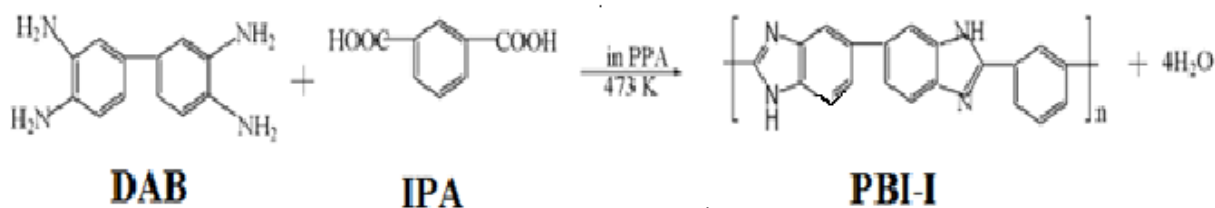
Scheme1: Synthesis of PBI from the monomer diaminobenzidene (DAB) and Isophthalic acid using polyphosphoric acid (PPA) as condensing medium

2.2 *Membrane Preparation:*

Dense membranes were prepared by solution casting method under identical conditions using 3% (w/v) polymer solution in DMAc, at 80°C for 14–18 h under dry atmosphere [1]. The solution after centrifugation at 3000 rpm (to remove undissolved particles, if any) was poured on a flat glass surface and heated at 80°C for 18 h under inert dry atmosphere. The thin film formed was peeled off and soaked in water at 60°C for 3 days in order to remove traces of DMAc. Such films were finally dried in vacuum oven at 100°C for a week and used for subsequent analyses. Four membranes of different thicknesses 65.2, 67.1, 78.1 and 91.6 micons were prepared.

2.3 *Doping of Membrane:*

Membrane samples of 4X4 cm^2 of different thickness were dipped in H_3PO_4 (PA) solution of various concentrations. The dip time required to achieve maximum possible doping was initially determined, and it was found that maximum possible doping was achieved by keeping the PBI-I membrane in the phosphoric acid (16.2 M) solution for various time intervals. The doped membranes were dried in the vacuum oven at 100°C for 3 days. The PA uptake (Mol/RU) was estimated gravimetrically. The H_3PO_4 (PA) uptake (Mol/RU) time required to achieve maximum absorption was ~ 14.2 (Mol/RU) (Fig.1).
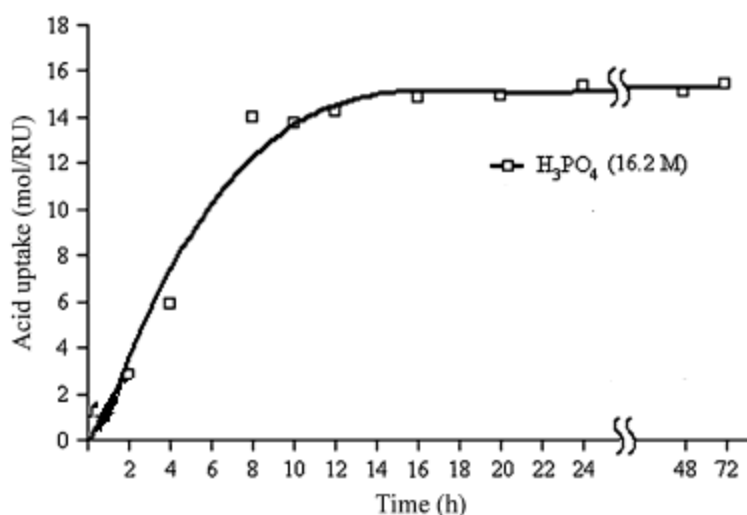

Fig. 1. H_3PO_4 uptake in PBI-I with time.

2.4 *Fabrication of Membrane Electrode Assembly (MEA):*

Two carbon cloths of size 5x5 cm^2 were made hydrophobic by imbibing them in 15% Teflon (PTFE) emulsion (Fuel cell stores Inc), followed by air drying for 30 min and further heat treated at 350°C for 5 h to adhere the PTFE with carbon cloth. Carbon ink was made by combining appropriate amount of Vulcan XC-72 carbon (Cabot Corporation) with PTFE emulsion in cyclohexane after ultrasonically mixing for 30 min. This ink was brushed on the carbon cloths till it reached the desired loading levels. The loading levels were double in the membrane facing side of the carbon cloth. These carbon cloths were cold pressed at 0.5 ton for 1 min and then kept in a furnace at 350°C for 30 min. Catalyst ink was prepared by adding 20% Pt/C and 1% PBI solution in DMAc. This mixture was ultrasonicated for 30 min and the resulting ink was brushed on the surface of the gas diffusion layer (GDL) in a hot plate until the desired loading was reached. On top of the catalyst layer a thin layer of PBI solution was given and the resulting electrodes were dried and hot pressed uni-axially with the PA doped PBI membrane. This MEA was kept in a desiccator for 1 day in order for the catalyst layer to become saturated with the excess of PA present in the membrane. All the MEAs were tested on an Arbin fuel cell test station (Model: Arbin-001 MITS Pro-FCTS 5.0-FCTS) under nonhumidified conditions.

Proton conductivity of the membranes was measured in the longitudinal direction with a four-probe method using a membrane conductivity cell (Bekktech) with gas flowing options. The membrane sample with an area of 1 cm × 3 cm was assembled in the cell in contact with two platinum electrodes placed at fixed positions. The H_2-O_2 flow at 1 atmospheric pressure was maintained at both electrodes. The potentiostat was set to apply specific voltages between two Pt electrodes, and the resulting current density was measured. The performance of the fuel cell was plotted in Fig. 2 to 5.

III.   Result And Discussion

It has been found that polybenzimidazole isolated from isophthalic acid (PBI-I) on doping with 16.2 molar H_3PO_4 at 298K for 20-24 hours or more absorbs maximum PA for proton exchange (PE) membranes use. The optimum PA concentration of 14.2 Mol/RU was achieved by variation of PA concentration. The membranes with doping level 4.08M, 5.44M, 7.48M and 10.88M PA per repeating unit having various thickness (65.2 – 91.6 micron) were subjected to polarization plot. The performance curves of PBI-I membrane of different thicknessare shown in Fig- 2,3,4 and 5. The performance reached maximum at 10.88 PA concentration (Mole/RU) having film thickness of 91.6 microns.

The inherent viscosity of polymer was determined using Ubbelohde viscometer with 0.2 g/dL polymer concentration in 98% H_2SO_4 at 35^oC, which was found 1dl/g. It was observed that power density increases with increasing membrane thickness. The current density also has the same trend. For the membrane having 10.88 Mol/RU gave OCV value 0.9V, the current density 1.76 A/cm^2 and power density of 450mw/cm^2 at 175^oC. The performance of cell membrane dropped enormously when ambient air was used in place of pure O_2 gas flow (Fig.5).

The critical studies of Fig- 2,3,4 & 5 shows the polarization plot for MEAs prepared from doped PBI-I membranes with different thickness as well as different doping level indicated that among four polarization plots having PBI-I membrane doping level 10.88 M/RU and thickness 91.6 Micron gave the best performance. This can be attributed to the fact that at lower doping level PBI-I membranes are not very good proton conductor and at higher doping level than 11M/RU there is leaching of phosphoric acid from membrane surfaces which ultimately affects the membrane performances. It is also inferred that membranes with lower thickness have low mechanical strength which is not suitable for H_2/O_2 fuel cell in long term performances.
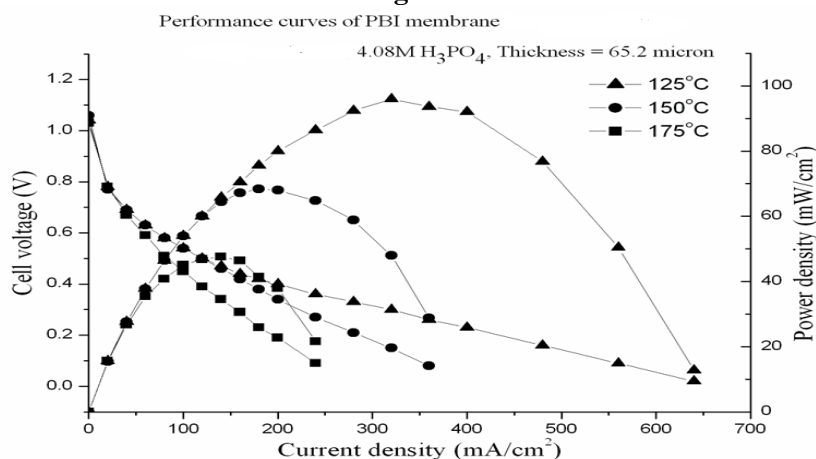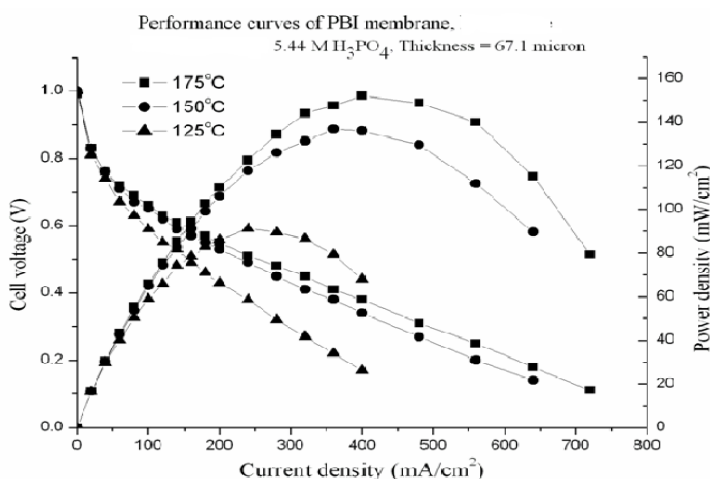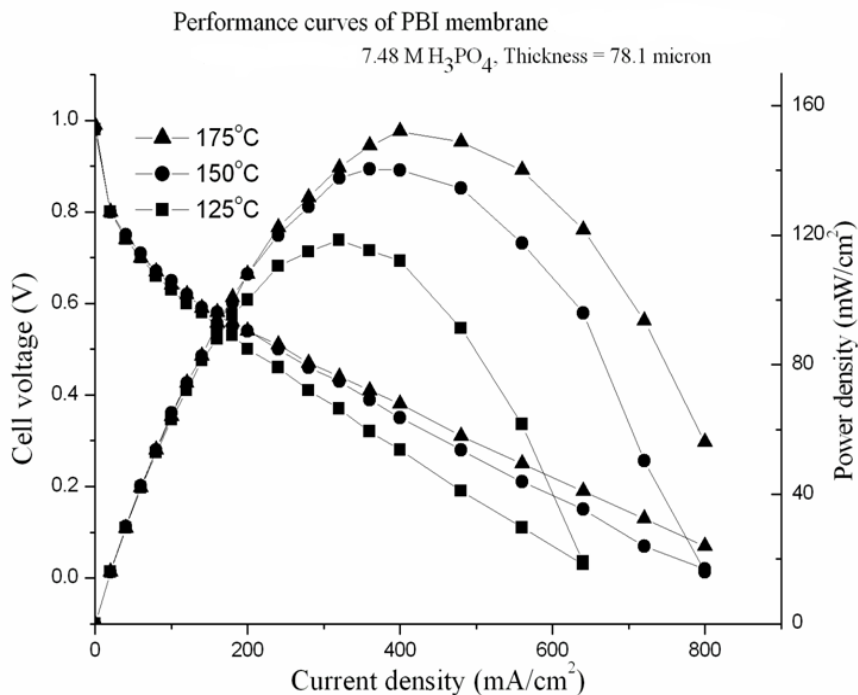
IV.   Figures

Fig-2

Fig-3

Performance curves of PBI membrane
7.48 M H_3PO_4, Thickness = 78.1 micron

Fig-4

Performance curves of PBI membrane
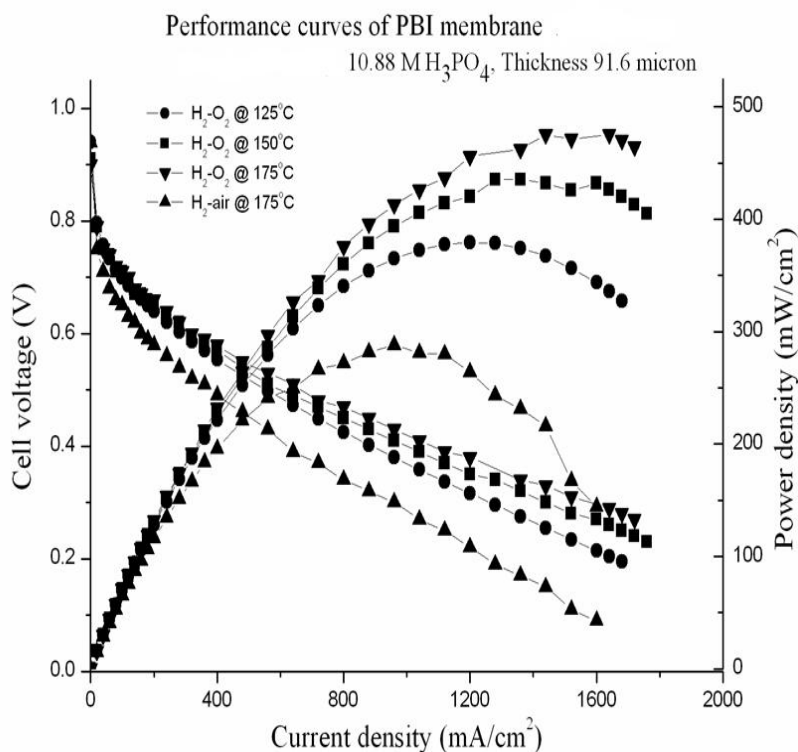10.88 M H_3PO_4, Thickness 91.6 micron

Fig-5

V. Conclusion

PBI-I doped membranes with 91.6 micron thickness and doping level of 10.88 H_3PO_4 (Mol/Ru) are good for H_2/O_2 fuel cell application as alternative ecofriendly green energy requirement .

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