

APPLICATION OF PHOSPHORIC ACID AND PHYTIC ACID DOPED  
POLYBENZIMIDAZOLE FOR HIGH TEMPERATURE PROTON EXCHANGE  
MEMBRANE FUEL CELL

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## **DEDICATION**

This thesis is dedicated to my parents and my family members for their endless supports and advices throughout this journey. Special thanks to my very supportive and understanding supervisors and lab mates who taught me to be responsible of my own decision and to always learn from the consequence of my decision and move on. Thank you.

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## ABSTRACT

An increase demand of energy supply has become the main concern since the conventional fossil fuels is exhaustive in supplies. Literature shows that proton exchange membrane fuel cell (PEMFC) has been receiving attention for various stationary and transportation application. Polybenzimidazoles-phosphoric acid (PBI/PA) has gaining attention to become a membrane for High Temperature Proton Exchange Membrane Fuel Cell (HT-PEMFC) applications. However, there have been concerns on the durability and stability of PBI/PA membrane system, which negatively affect their widespread used for commercialization. The problems include the PA leaching from PEM that lead to proton conductivity decay as well as deterioration of PEMFC performance during long-term operation. Therefore, the aim of this research is to develop a new PBI/Acid membrane containing highly phosphonated phytic acid (PyA) ( $C_6H_{18}O_{24}P_6$ ) molecules as a co-dopant acid of PA. The presence of abundance hydrophilic hydroxyl groups around the cyclohexane ring of PyA molecule is expected to be able to participate in H bonding interactions with the functionalities in PBI/PA matrix and hence help to improve its stability and durability. The analyses of this newly PBI/Acid membrane system were carried out using Fourier- transform infrared (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Based on the analysis, the synthesized PBI doped acid membrane followed the required properties for HT-PEMFC application, which is stable up to 500 °C, in which significantly higher than the operating temperature of HT-PEMFC. To address the issue on proton conductivity decay, PBI membranes with different porosity were fabricated as a sponge-like porous structure membrane has the ability to the absorb excess acids. Porous PBI-1 (pPBI-1) and porous PBI-5 (pPBI-5) membranes which represent 1 wt% and 5 wt% additional of porogenic solvent were successfully fabricated. Six different acid doping conditions, which varied time and temperature were applied and the acid doped membranes were evaluated based on their acid doping level (ADL) behaviour with respect to the proton conductivity value. The results showed that porous PBI membrane with higher porosity contributed to higher ADL values, which resulted in higher proton conductivity value. In addition, the membrane were tested under different relative humidity (RH), and the results indicate that the proton conductivity increases significantly with RH and temperature. Subsequently, the single cell test of HT-PEMFC was conducted and the performance of the selected doping condition of porous PBI/Acid doped membranes (from doping Condition 6) was evaluated following the requirement of HT-PEMFC operation. The performance of the membranes tested for HT-PEMFC showed that porous PBI membrane with lower porosity exhibiting better performance than the porous PBI membrane with higher porosity. Therefore, it can be concluded that both pPBI-1 and pPBI-5 gave an excellent performance in their respective ways and based on the membrane evaluation performance, PBI membrane doped with both PA and PyA have the potential to be used as a doping solution for HT-PEMFC.

## ABSTRAK

Permintaan yang tinggi terhadap sumber tenaga telah merunsingkan pelbagai pihak kerana sumber konvensional seperti tenaga fosil dijangka tidak dapat bertahan lama. Tinjauan literatur menunjukkan penggunaan Sel Bahan Api Membran Penukaran Proton (PEMFC) kini semakin mendapat perhatian kerana kepelbagaian aplikasi yang boleh digunakan seperti dalam bidang pengangkutan dan penyimpanan tenaga. Membran polibenzimidazol-asid fosforik (PBI/PA) mula mendapat perhatian untuk digunakan dalam aplikasi PEMFC yang bersuhu tinggi (HT-PEMFC). Walaubagaimanapun membran PBI/PA turut mempunyai kekurangan dari segi ketahanan dan kestabilan. Antara masalah yang dialami termasuklah kebocoran asid dari PEM dan seterusnya mengakibatkan proton konduktiviti dan prestasi PEMFC untuk jangka masa panjang terjejas. Oleh itu, objektif utama kajian ini dibuat adalah untuk menghasilkan membran PBI berasaskan PEM yang mengandungi asid fitik yang berfosfonasi tinggi bersama-sama asid fosforik sebagai asid bersama. Dengan kehadiran kumpulan hidrofilik dan hidroksil di dalam asid fitik dijangka dapat memperbanyakkan lagi ikatan hidrogen antara matriks PBI/PA, dan seterusnya dapat memperbaiki kestabilan dan ketahanan membran. Analisis- analisis telah dibuat menggunakan Fourier Transform Inframerah (FTIR), Pembelauan Sinar-X (XRD) dan Analisis Termogravimetrik (TGA). Berdasarkan analisis yang dijalankan, asid didopkan PBI membran yang disintesis mengikut ciri-ciri yang diperlukan untuk aplikasi HT-PEMFC iaitu stabil sehingga suhu 500 °C, di mana suhu ini lebih tinggi daripada suhu operasi HT-PEMFC. Untuk mengatasi masalah proton konduktiviti yang rendah, membran PBI dengan pelbagai keliangan telah berjaya dihasilkan sebagai seperti span yang mempunyai kemampuan untuk menyerap asid berlebihan. Membran-membran tersebut dikenali sebagai membran PBI dengan tahap 1% (pPBI-1) keliangan dan membran PBI dengan tahap 5% keliangan. Enam keadaan pendopan asid yang berbeza masa dan suhu telah digunakan dan membran dinilai berdasarkan tahap pendopan asid (ADL) dengan mengikut kepada nilai proton konduktiviti bagi membran. Hasil kajian menunjukkan semakin tinggi keliangan membran, semakin tinggi ADL dan semakin tinggi nilai proton konduktiviti bagi membran. Tambahan lagi, membran diuji mengikut kelembapan relative (RH) dan keputusannya menunjukkan proton konduktiviti meningkat mengikut RH dan suhu. Kemudian, operasi sel tunggal untuk membran yang terpilih iaitu dari keadaan nombor 6 telah dijalankan mengikut kehendak operasi HT-PEMFC. Hasil penilaian membran yang dijalankan menunjukkan bahawa membran berkeliangan rendah pula yang memberikan prestasi yang lebih baik. Kesimpulannya bahawa kedua-dua membran pPBI-1 dan pPBI-5 memberikan prestasi yang baik dalam penilaian membran masing-masing iaitu dalam proton konduktiviti dan operasi sel tunggal berasaskan HT-PEMFC PBI dengan membran asid dopan fitik asid mempunyai potensi untuk digunakan sebagai cecair dopan asid dalam operasi HT-PEMFC.

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## LIST OF ABBREVIATIONS

PEMFC	-	Proton Exchange Membrane Fuel Cell
HT-PEMFC	-	High Temperature Proton Exchange Membrane Fuel Cell
GDL	-	Gas Diffusion Layer
PBI	-	Polybenzimidazole
PFSA	-	Perfluorinated Sulfonic Acid
LT-PEMFC	-	Low Temperature Proton Exchange Membrane Fuel Cell
PA	-	Phosphoric Acid
PyA	-	Phytic Acid
ORR	-	Oxygen Reduction Reaction
FTIR	-	Fourier-Transform Infrared Spectroscopy
XRD	-	X-Ray Diffraction
SEM	-	Scanning Electron Microscopy
RH	-	Relative Humidity
MEA	-	Membrane Electrode Assembly
TGA	-	Thermal Gravimetric Analysis
FCHE	-	Fuel Cell and Hydrogen Energy Association
CHP	-	Combined Heat and Power
UPS	-	Uninterrupted Power Supply
APU	-	Auxiliary Power Unit
ICE	-	Internal Combustion Energy
GO	-	Graphene Oxide
PPA	-	Polyphosphoric Acid
DBP	-	Dibutyl Phthalate
DMAc	-	Dimethylacetamide
ADL	-	Acid Doping Level
MTS	-	Membrane Test System
FC	-	Fuel Cell
ASR	-	Area Specific Resistance

$R_{HF}$	-	High Frequency Intercept
pPBI-1	-	Porous PBI-1 wt%
pPBI-5	-	Porous PBI-5 wt%
UTM	-	Universiti Teknologi Malaysia
MJIIT		Malaysia-Japan International Institute of Technology

## LIST OF SYMBOLS

wt%	-	Weight percent
rpm	-	Revolution per minute
mS/cm	-	MilliSiemens per centimetre
$2\theta$	-	Angle unit
A/cm <sup>2</sup>	-	Current density
W/cm <sup>2</sup>	-	Power density

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

The global expansion of industries and technologies has resulted in a slew of environmental challenges, including increased air pollution and global warming as carbon dioxide emissions continue to climb. Furthermore, rising energy demand from developing countries has become a major problem, as traditional fossil fuels will not last more than a century and production is frequently hampered by geopolitical concerns. Various research and development (R&D) activities on renewable energy resources and technology have been spurred by the uncertainty of energy supply and environmental pollution challenges.

The global renewable energy installation has been progressing since 2007 till 2017, according to the World Total Energy Supply in 2019. The trend is projected to continue in the future, as demand for low- and zero-emission energy sources grows, particularly in developed and emerging countries. In this context, green hydrogen energy, or hydrogen fuel cells, is currently in demand since it is more ecologically benign and less expensive than other renewable energy sources.

A fuel cell is an electrochemical device that uses electrochemical oxidation of fuel at the anode and reduction of oxidant at the cathode to convert chemical energy from fuel into electrical energy (Li, 2014). Fuel cells have various advantages over conventional energy conversion systems such as internal combustion engines and batteries. These benefits include a wide range of fuel options (e.g., hydrogen, methane, and methanol), the capacity to create continuous power as long as the reactants are replenished, high energy conversion efficiency (up to 80%), and environmental friendliness (water is the sole chemical by-product) (Chen et al, 2009). Above all, researchers believe that fuel cells have the potential to reduce our reliance on fossil



fuels, making them a clean and promising alternative to traditional technologies for utilising hydrocarbon fuel resources in a variety of applications ranging from portable power to transportation and stationary power systems.

Distinct principles, such as the type of electrolyte used in the cell, operating temperatures, charge carrier, and target applications, have been used to build various types of fuel cells. Proton Exchange Membrane Fuel Cell (PEMFC), Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell are the distinct types of fuel cells based on their varied electrolyte materials (SOFC). Table 1.1 (Energy Efficiency & Renewable Energy (EERE), 2011) displays the various types of fuel cells and their features.

Due to its comparatively high power density, low operating temperature, and quick start-up capability, PEMFC has attracted the most attention among the aforementioned types of fuel cells above, especially for automotive and small stationary applications (Song et al, 2008). PEMFCs are a promising technology in the twenty-first century, providing consumers with a clean and efficient power generating source. The first PEMFC unit was designed by General Electric (GE) researcher William Thomas Grubb in the late 1950s, and the device was then refined by another GE researcher, Leonardo Niedrach, by adding platinum as a catalyst on the membrane (Li, 2014). The structure of a PEM fuel cell is depicted in Figure 1.1. It comprises of a proton exchange membrane sandwiched between two Pt catalyst-loaded gas diffusion electrodes, a gas diffusion layer (GDL), and a bipolar plate with flow channels on both the anode and cathode (Zhou, 2015)

Table 1.1 Comparison of Fuel Cell Technologies (EERE, 2011).

Fuel Cell Type	Abbreviation	Electrolyte Materials	Conductive ions	Operating Temperature	Typical Stack Size	Electrical Efficiency (LHV)	Applications
Proton Exchange Membrane Fuel Cell	PEMFC	Proton exchange membrane	H <sup>+</sup>	50-100 °C, typically 80 °C	<1 kW-100 kW	60% direct H <sub>2</sub> 40% reformed fuel	<ul style="list-style-type: none"> <li>• Backup power</li> <li>• Portable power</li> <li>• Distributed generation</li> <li>• Transportation</li> <li>• Specialty vehicles</li> </ul>
Anion Exchange Membrane Fuel Cell	AEMFC	Alkaline anion exchange membrane	OH <sup>-</sup>	30-90 °C, 80-100%RH	<1 kW-100 kW	60%	<ul style="list-style-type: none"> <li>• Vehicles</li> </ul>
Solid Oxide Fuel Cell	SOFC	Ceramic	O <sup>2-</sup>	500-1000 °C	1 kW-2 MW	60%	<ul style="list-style-type: none"> <li>• Auxiliary power</li> <li>• Electric power</li> <li>• Distributed generation</li> </ul>
Alkaline Fuel Cell	AFC	Aqueous alkaline solution	OH <sup>-</sup>	90-100 °C	1-100 kW	60%	<ul style="list-style-type: none"> <li>• Military</li> <li>• Space</li> </ul>
Phosphoric Acid Fuel Cell	PAFC	Immobilized phosphoric acid	H <sup>+</sup>	150-200 °C	5-400 kW, 100 kW Module (liquid PAFC)	40%	<ul style="list-style-type: none"> <li>• Distributed generation</li> </ul>
Molten Carbonate Fuel Cell	MCFC	Immobilized liquid molten carbonate	CO <sub>3</sub> <sup>2-</sup>	600-700 °C	300 kW- 3 MW 300 kW module	45-50%	<ul style="list-style-type: none"> <li>• Electric utility</li> <li>• Distributed generation</li> </ul>

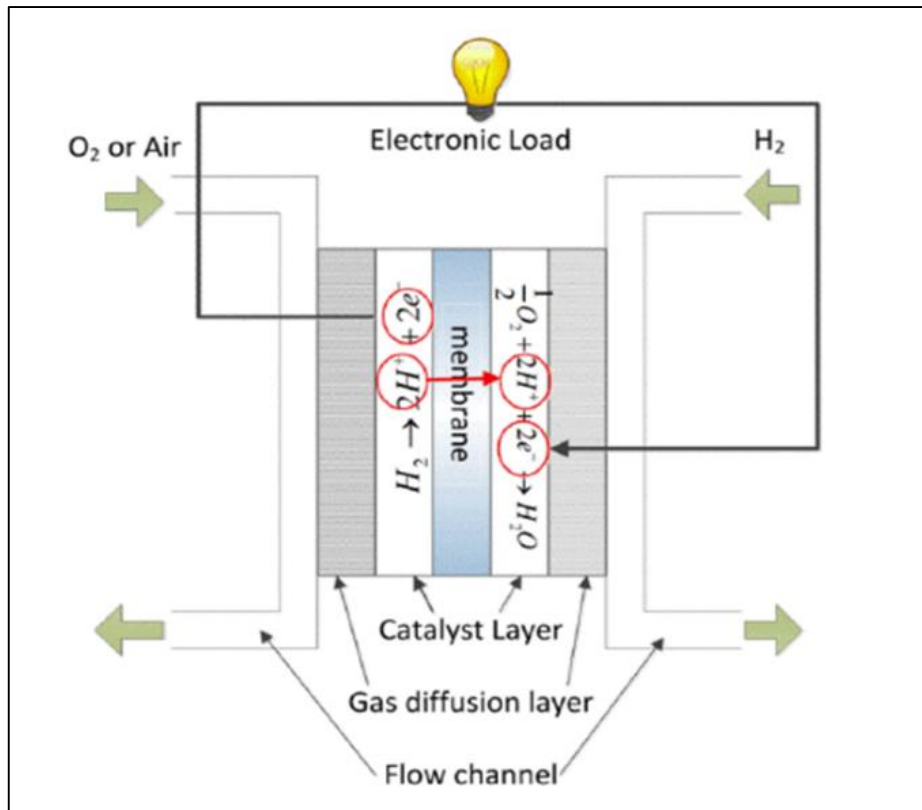


Figure 1.1 The structure and operational principle of PEM fuel cell (Zhou, 2015)

PEMs with strong proton conductivity, low electronic conductivity, low permeability of fuel gases, low electroosmotic drag coefficient, good temperature resistance, high chemical stability, good mechanical qualities, and low cost have all been developed for use in fuel cell systems (Peighambardoust et al, 2009). PEMFCs have traditionally been based on perfluorinated sulfonic acid (PFSA) membranes, which have a perfluorinated backbone similar to polytetrafluoroethylene (PTFE, Teflon®) and pendant perfluorinated side chains linked to the main chain by ether bonds, as well as sulfonic acid groups at the end of these pendant chains. Among these, the Nafion® membranes family, which includes the PFSA membrane, is the most widely investigated. PFSAs' functioning window in the PEMFC is limited to temperatures below 100 °C (usually at 80 °C) despite its exceptional stability. The operation of PEMFCs at such low temperatures (LT-PEMFC) poses a number of technical obstacles, including keeping the membranes fully hydrated to achieve high proton conductivity via a humidification system, the need for very pure hydrogen supply, and the high cost of PFSA membranes (Asensio et al, 2010).

As a result of these disadvantages, more study into the development of PEMs for high temperature operation (HT-PEMFC) in the normal range of 100 to 200 °C is required. The next generation of fuel cell technology is known as HT-PEMFC. This is owing to the cost savings and reliability of LT-PEMFC in addressing various challenges, including enhanced reaction kinetics, impurity tolerance in the hydrogen feed, and the ability to use low-cost catalyst in the anode, heat rejection, and water management (Rosli et al, 2017). Acid-doped polybenzimidazole (PBI) membranes were used in the majority of HT-PEMFC studies. PBI is generally less expensive than PFSA and is thermally and chemically stable under a variety of circumstances. Acids including hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), perchloric acid (HClO<sub>4</sub>), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) might theoretically be combined with PBI to create acid-base (PBI) complex membrane systems. Phosphoric acid (PA) doped PBI membranes, in particular, shown excellent proton transport capabilities, allowing them to be employed in PEMFCs at temperatures as high as 200 °C with little or no humidification (Li et al, 2004). Furthermore, PA is naturally proton conductive and thermally stable, with a low vapour pressure at high temperatures (Bose et al, 2011). In the last decade, great research and development activity on HT-PEMFCs based on PA-PBI have resulted from these advantages. However, questions about the durability and stability of such PEMFCs in long-term fuel cell applications hampered their wider adoption. In more detail, the issues stem from PA leaching from PEM, which produces inhomogeneous PA distribution, resulting in proton conductivity degradation and subsequent decrease of PEMFC performance over time.

PBI-PA membranes have been found to degrade due to PA leaching on several occasions. According to Leykin et al. (2010), the majority of acid escapes the membrane during the first 10 minutes because it is not chemically attached to the polymer but is held in the polymer by relatively weak hydrogen bonding and dipole interaction. As a result, over-stoichiometric levels of acid were extracted quickly. As a result of this issue, there was an inhomogeneous PA distribution, which reduced proton conductivity and impaired PEMFC performance over time (Berber et al, 2013). Furthermore, because Pt catalyst is poisoned by chemisorbed dihydrogen phosphate (H<sub>2</sub>O<sub>4</sub>P<sup>-1</sup>) and hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>) ions, leaching of PA could reduce the oxygen reduction reaction (ORR) activity of Pt-based cathodes (Li, 2014). The slow kinetics of ORR and the transport constraints of protons and reactants at the cathode,

according to Su et al (2013), severely hampered the cell performance of PEMFCs operating at high temperatures.

Alternative membranes with tightly bonded functional groups are required to solve the PA leaching problem caused by PBI. As a result, instead of phosphoric acid, this research focuses on membranes with highly phosphonated phytic acid ( $C_6H_{18}O_{24}P_6$ ) molecules as a dopant. The bulky multi-phosphonated molecules with an abundance of hydrophilic hydroxyl groups around the cyclohexane ring are thought to be able to strongly participate in interactions with the functionalities in the PBI matrix, reducing the risk of leaching and improving its stability and durability, especially for long-term use. The focus of research is on creating manufacturing methods for introducing large amounts of phytic acid molecules and evaluating acid doping ability, mechanical properties, oxidative stability, and long-term performance in HT-PEMFCs.

## **1.2 Problem Statements**

Previous studies showed that, the PFSA membrane consist of PTFE backbone is more compatible used in LT-PEMFC compared to HT-PEMFC. This is because at high temperature, the proton conductivity of PFSA membrane is decreasing due to their glass transition temperature ranging from 120 to 140 °C and the evaporation of water molecules which responsible for proton conduction is happened (Haider et al, 2021).

Therefore, modified PFSA membrane have been gaining attention and more research have been done to make PFSA membrane applicable for high temperature application. These including the incorporation of hygroscopic inorganic materials like  $SiO_2$  nanoparticles (Xu et al, 2020), graphene oxide, and ionic liquids (Díaz et al, 2014), inorganic hetero poly acids like phosphotungstic acid (PTA) (Liu et al, 2020), and layered double hydroxide nanoparticles (Nicotera et al, 2014). Despite these modification is successfully improved the performance of ionic conductivity and meet

the precondition for use in HT-PEMFCs based on their thermal gravimetric analysis, however, the operating temperature of modified PFSA membranes is still not high enough to satisfy the requirement for HT-PEMFC because most of them can only work smoothly in the temperature range from 100 to 120 °C and high humidity level is still required to maintain high proton conductivity at high temperature for HT-PEMFC operation (Haider et al, 2021).

Although the operating PEMFC at high temperature has many advantages and attractive features, there are several challenges associated with HT-PEMFC that need to be overcome before their further commercialization. These include (i) low acid doping level and low conductivity at dry conditions, (ii) acid leaching from membrane, and (iii) poisoning of catalyst by PA.

Particularly, the conductivity of PBI/PA membrane greatly depends on the level of acid doping where PBI/PA membrane exhibit high conductivity only with high acid loadings, at least higher than 3.0 PA molecules per repeats unit of PBI. However, excess PA content would negatively affect the mechanical strength and leaching especially at higher temperature (Xu et al, 2011). This situation results in a reduction of conductivity and fuel cell performance and causing the free acid to poison the electrocatalyst at the cathode as discussed earlier.

Despite the improvement in the aforementioned limitations by some modifications on the polymers structure and the use of composite membranes (Abouzari et al, 2019), acid leaching from PBI/PA materials is still a serious concern that lead to serious degradation of fuel cell components, which in turn affect the power density and performance of the fuel cell especially for long term operation. In this research, PBI based PEM membrane doped with a highly phosphonated phytic acid was developed as a regard to overcome the acid leaching from PBI/PA membrane.

### 1.3 Research Objectives

The main aim of this research is to develop a new PBI-based PEM membrane containing highly phosphonated phytic acid ( $C_6H_{18}O_{24}P_6$ ) molecules with low acid leaching characteristics for HT-PEMFC. Details of the research objectives are as follows:

- i. To investigate the effect of different porosity of PBI membrane toward different conditions of acid doping
- ii. To characterize the physicochemical properties of acid doped PBI with respect to the HT-PEMFC.
- iii. To evaluate the performance of acid doped PBI membrane in HT-PEMFC under control condition; such as temperature and relative humidity.

### 1.4 Research Scope

To achieve the above mentioned objective, the following scope has been considered.

1. Preparation of new phytic acid doped PBI membrane using various doping conditions which divided into two phase; phase 1, direct doped of porous PBI membrane with the mix of PA and PyA solution with ratio (1:1) and the doping procedure were varied in terms of the temperature and immersion time. In phase 2, doping of porous PBI membrane with PA, then followed by doping with PyA under different temperature and immersion time.
2. Establishing relationship between the applied membrane doping condition and acid doping level with proton conductivity of membranes.

3. Evaluation of PBI/acid based membrane properties with respect to HT-PEMFC requirements. Several characterization methods such as Fourier-Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). The through plane membrane resistance and conductivity of developed membranes were evaluated as a function of temperature and humidity level.
4. Preparation of the membrane electrode assembly (MEA) by hot-pressing of commercial gas diffusion electrodes on the doped PBI/PyA membrane. The cell was constructed using bipolar plates in serpentine pattern Z-type gas flow configuration.
5. Evaluation of acid doped membranes of various doping levels performance in HT-PEMFC in order to find the optimum acid-doping level and doping condition. The performance of developed membranes were evaluated at temperature range of 100-160 °C and low relative humidity (0-10% relative humidity (RH)).

## **1.5 Significance of Study**

Phytic acid can potentially replace PA and lead to some advantages in the HT-PEMFC including low leaching and enhanced performance. Despite such advantage, there are only a few studies addressing the behaviour of PBI membranes doped with phytic acid in HT-PEMFC application.

However in this study, PyA was used as a co-dopant acid of PA. This is due to the PyA molecules have a big molecule that prevent PyA to be loaded fully into the PBI matrix. Therefore, PA was introduced first as a dopant since PA has small size of molecules compared to PyA, hence more acid molecules can be load in the PBI structure and form a big molecule of PBI/PA at the first layer. Then, this big molecule of PBI/PA make the big molecule of PyA possible to be loaded into the structure and form PBI/PA/PyA. With the presence of PyA as a capping in the second layer of PBI/PA/PyA managed to form more H<sub>2</sub> bonding between them and resulting in the



formation of network-like and proton hopping pathway, then synergize the conductivity in the polymer. Having of 6 acid groups in one molecule is expected to effectively interact with PBI matrix hence, improved its stability and durability especially for long term operation.

In this study, a simple and cost effective technique were employed for further improve the efficiency of the membrane by implying various acid doping conditions in order to search an optimum acid-doping level of the membrane. This modification and improvement is believed to reduce the cost of maintenance system as well as improving the performance of the fuel cell operating at high temperature (100-160 °C) and low relative humidity (0-10% RH).

## **1.6 Thesis Outline**

This thesis is divided into four chapters. Chapter 1 explained the research background, problem statement, objectives, research scopes and significance of the present study. Chapter 2 discussed the principle of PEM and focuses on the potential of HT-PEM in fuel cell application. In addition, the techniques used to modify the PBI/PyA membrane is also explained together with the previous study towards other applications. In Chapter 3, experimental work is addressed in detail. Materials and equipment are also introduced. The results obtained in this work concerning the membrane characterization, membrane evaluation and performance of modified PBI membranes with respect to HT-PEMFC are presented, analysed and discussed in Chapter 4. Finally, the findings from this research is summarized in Chapter 5 and some recommendation for the improvement of the research interest is also included.

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