

CARBON SUPPORTED PALLADIUM-PLATINUM CATALYST FOR OXYGEN
REDUCTION REACTION IN HIGH TEMPERATURE PROTON EXCHANGE
MEMBRANE FUEL CELL

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A special dedication to ayah, Yusof Hassan

Thank you for the endless support during my ups and downs even though you are no longer here to see me put an end for another chapter of my life stories

To mak, Saoyah Abdul Rahman,

Thank you for always being here; your endless love, faith and encouragement never fail to strengthen me

To my beloved siblings,

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To my love,

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To the light of happiness,

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ABSTRACT

Platinum (Pt) is the most commonly adopted electrocatalyst for oxygen reduction reaction in proton exchange membrane fuel cells (PEMFCs) due to its noteworthy features. However, for PEMFCs to have wide practical applications and become commercially viable, the challenging issue of the high catalyst cost, resulting from the exclusive conventional practice of platinum based catalysts should be addressed. Therefore, a study of the palladium (Pd) as a partial substitution to the platinum on carbon (C) has been conducted in high temperature PEMFCs. A series of metal electrocatalyst (Pt/C, Pd/C, and 10-40 wt% Pt-Pd/C) were synthesized via chemical reduction method and their characteristics have been observed by cyclic voltammetry, linear sweep voltammetry, field emission scanning electron microscope and energy dispersion x-ray, Fourier transform infrared spectroscopy, x-ray diffraction and nitrogen-physorption. Among all, 30 wt% Pt-Pd/C, gave a promising 0.9 Wcm^{-2} power density at $170 \text{ }^\circ\text{C}$. 30 wt% Pt-Pd/C was then nominated to further enhance the catalyst layer. Polybenzimidazole (PBI) was added onto the catalyst layer of 30 wt% Pt-Pd/C in order to increase the porosity and facilitate the transport of oxygen in the catalyst layer due to their hydrophobic properties. The PBI ratio was varied towards 30 wt% Pt-Pd/C (PBI: 30 wt% Pt-Pd/C; 1:99, 3:97, 5:95 and 9:91). Short-term durability for all catalysts was conducted from 24-96 hr revealed that the impedance curves of 5:95 catalysts showed the slowest performance decay of the membrane electrode assembly (MEA). Hence, this result indicated that the decay of the catalyst could be prevented by appropriate PBI loading as well as increasing the lifetime of the MEA. The 5:95 MEA delivered a peak power density of 1.30 Wcm^{-2} , corresponding to an overall Pt utilization $0.02 \text{ mg}_{\text{Pt}}/\text{cm}$. At $170 \text{ }^\circ\text{C}$, the MEA cathodic catalyst utilization was $65 \text{ kW/g}_{\text{Pt}}$. This is 1.5 times higher than the Pt-utilization efficiency of a reference fuel cell prepared using commercial catalyst layer, which emphasizes the enhancement that was mainly attributing by the Pd substitution and PBI ionomer in the catalyst. All the result indicated in this study strongly motivate the application of combining suitable ratio of PBI binder in an optimum metal loading catalyst. This combination would produce a low resistance MEA in order to compensate an encouraging power density.

ABSTRAK

Platinum (Pt) sering digunakan sebagai elektromangkin bagi tindakbalas pengurangan oksigen di dalam sel-sel bahanapi membran tukaran proton (PEMFCs) disebabkan oleh ciri-cirinya yang menarik. Walau bagaimanapun, bagi penggunaan PEMFCs yang lebih meluas secara praktikal dan menjadi berdaya maju komersial, cabaran terhadap isu kos mangkin yang tinggi dihasilkan dari penggunaan eksklusif mangkin berasaskan platinum secara konvensional harus diutarakan. Maka, satu kajian menggunakan paladium (Pd) sebagai sebahagian penggantian kepada Pt di atas karbon (C) telah dijalankan pada suhu tinggi PEMFCs. Satu siri elektromangkin logam (Pt/C, Pd/C, dan 10-40 wt% Pt-Pd/C) telah disintesis melalui kaedah pengurangan kimia dan ciri-cirinya diperhatikan melalui kitaran voltammetri, lengkungan linear voltammetri, mikroskop elektron pengimbas pancaran medan-sinar-x tenaga serakan, spektroskopi infra-merah transformasi Fourier, pembelauan sinar-x dan fisierapan nitrogen. Antara semua, 30 wt% Pt-Pd/C telah menghasilkan 0.9 Wcm^{-2} ketumpatan kuasa pada suhu 170°C . 30 wt% Pt-Pd/C seterusnya dicalonkan bagi meningkatkan lagi lapisan mangkinnya. Polibenzimidazola (PBI) ditambah pada lapisan mangkin 30 wt% Pt-Pd/C bagi menambahkan lagi keliangan dan membantu pergerakan oksigen di dalam lapisan mangkin yang disebabkan oleh sifat hidrofobiknya. Kajian dipelbagaikan dengan kadar PBI terhadap 30 wt% Pt-Pd/C (PBI: 30 wt% Pt-Pd/C; 1:99, 3:97, 5:95 and 9:91). Ujian ketahanan jangka pendek untuk semua mangkin dijalankan pada sekitar 24-96 jam menunjukkan keluk galangan mangkin 5:95 adalah paling lambat prestasi pereputan himpunan elektrod membran (MEA). Oleh yang demikian, keputusan ini menunjukkan bahawa pereputan mangkin boleh dielakkan dengan menggunakan kandungan PBI yang betul dan juga mampu memanjangkan jangka hayat MEA. MEA 5:95 menghasilkan 1.30 Wcm^{-2} ketumpatan kuasa terhadap $0.02 \text{ mg}_{\text{Pt}}/\text{cm}$ penggunaan keseluruhan Pt. Pada 170°C , penggunaan katod MEA adalah sebanyak $65 \text{ kW/g}_{\text{Pt}}$. Ini adalah 1.5 lebih tinggi daripada kecekapan sel bahanapi rujukan yang disediakan menggunakan lapisan mangkin yang komersial di mana ianya menekankan peningkatan utama adalah disebabkan penggantian Pd dan pengenalan ionomer PBI ke dalam lapisan mangkin. Keputusan ini merangsang kuat penggunaan gabungan nisbah perekat PBI yang sesuai di dalam mangkin muatan logam optimum. Gabungan ini mampu menghasilkan rintangan MEA yang rendah bagi meningkatkan lagi ketumpatan kuasa.

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LIST OF ABBREVIATIONS

10 wt% Pt-Pd/C	-	10 wt% of Pt-Pd loaded on carbon using chemical reduction method
20 wt% Pt-Pd/C	-	20 wt% of Pt-Pd loaded on carbon using chemical reduction method
30 wt% Pt-Pd/C	-	30 wt% of Pt-Pd loaded on carbon using chemical reduction method
40 wt% Pt-Pd/C	-	40 wt% of Pt-Pd loaded on carbon using chemical reduction method
PEMFC	-	Proton exchange membrane fuel cell
HT-PEMFC	-	High temperature proton exchange membrane fuel cell
LT-PEMFC	-	Low temperature proton exchange membrane fuel cell
MEA	-	Membrane electrolyte assembly
GDL	-	Gas Diffusion Layer
GE	-	General Electric
FESEM-EDX	-	Field Emission Scanning Electron Microscope-Energy Dispersion X-ray Spectrometer
FTIR	-	Fourier Transform Infrared Spectroscopy
XRD	-	X-Ray Diffractometer

LIST OF SYMBOLS

W	-	Watt
kW	-	kiloWatt
°C	-	Degree celcius
°	-	Degree
hr	-	Hour
\$/kW	-	currency
%	-	Percentage
cm	-	Centimeter
eV	-	Electron Volt
F	-	Faraday constant which the amount of electric carried out by 1 mole of electrons
g	-	Gram
g L ⁻¹	-	Gram per liter
I	-	Current in unit ampere
K	-	Kelvin
mA	-	Milliamphere
min	-	Minute
mg L ⁻¹	-	Milligram per liter
mL	-	Milliliter
M	-	Molar
nm	-	Nanometer
s	-	Second
W g ⁻¹	-	Watt per gram

CHAPTER 1

INTRODUCTION

1.1 Research Background

Today, we are facing a severe challenge such as global warming and climate change due to the usage of fossil fuels. Fossil fuel such as natural gases and petroleum oil are classified as non-renewable energy resources that are difficult to be replaced in a short period of time after being utilized and should be replaced by other promising alternative sources. The greenhouse gas emissions are also mainly derived from the transportation sector and electricity power generation based on fossil fuel sources. Therefore, a global solution taken must involve a dramatic shift to practical and environmentally sustainable energy sources. In the interest of the extending concerns on the consumption of petroleum based energy resources and also the changes in climate pattern, alternatives energy power generation has been discovered in recent years (Sims, 2014).

High capacity energy systems, such as fuel cells are highly desirable to meet the urgent requirement of electric vehicles and utilization of sustainable energies (Bruce *et al.*, 2012). Fuel cells due to their particular properties are on the track in creating vast revolutionary modification in the electricity production field. By definitions, fuel cell is an electrochemical device in which the chemical energy of fuel in the absence of fuel combustion converted to electrical energy. Therefore, in a

fuel cell system, the chemical energy related to electrochemical reaction of the fuel with oxidant directly change into the water, electricity and heat (Peighambardoust *et al.*, 2010). Currently, from different types of fuel cells, proton exchange membrane fuel cell (PEMFC) which is characterized by its fast start up and low operation temperature has been received a lot of attention (Othman *et al.*, 2012). PEMFCs are also have been considered to be a promising technology for clean and efficient power generation.

However, PEMFC possess several disadvantages. For example, the low operating temperature PEMFC (LT-PEMFC) has a very low tolerance to impurities that present in fuel, thus requiring 99% pure hydrogen which is very costly. The heat produced from the LT-PEMFC is also a low temperature and thus is difficult to transfer away for use in other processes. A water management system is needed to prevent flooding/drying out of the membrane electrode assembly (MEA) due to the nature of the membrane which lead to a loss in a performance (Chandan *et al.*, 2013). Thus, PEMFC system complexity could be reduced by the development of water-free electrolytes membrane that does not require hydration. It also enables the PEMFC to be operated under warm conditions (100-200°C) thus further improving its efficiency. In simple words, these issues can be overcome through the use of a high temperature PEMFC (HT-PEMFC).

As such, during these recent years, there has been an intense research activity in order to improve all the components in HT-PEMFCs especially in membrane electrode assembly (MEA) (Lobato *et al.*, 2010). Highly dispersed carbon-supported Pt particles for MEA are the characteristics of the present benchmark electrocatalysts for HT-PEMFCs. Ultra low Pt loading (0.05-0.3 mgcm⁻²) electrodes have been developed. Yet, the continuous increase of the cost of platinum has made less effective such progresses. In the transition process from platinum to cheaper non platinum-group (NPG) metals or non-precious catalysts by total or partial substitution, palladium-based substitution electrocatalysts may represent a proper compromise due to its lower cost and abundance (Stassi *et al.*, 2013).

Recently, for other modification in MEA, several researchers have used different polymers to act as binders in the catalyst layer for HT-PEMFCs, such as polytetrafluoroethylene (PTFE) (Su *et al.*, 2013; Oono *et al.*, 2012; Oono *et al.*, 2010; Wannek *et al.*, 2009), polyvinylidene fluoride (PVDF) (Su *et al.*, 2013; Liang *et al.*, 2014), and Nafion (Su *et al.*, 2013; , Modestov *et al.*, 2009). From these studies, it was observed that when PTFE and PVDF, serving as a binder, are introduced into the catalyst layer, porosity is enhanced, and the transport of oxygen in the catalyst layer is facilitated because of their hydrophobic properties.

Unfortunately, to date, no study is reported on the use of between coupled Pt-Pd together with PBI on performance have not been investigated for HT-PEMFCs. Therefore, the main aim of this work is to study the partial substitution of palladium on platinum catalyst with the presence of PBI as a binder. In this study, black Vulcan Carbon Xc-72 was employed as the support to deposited platinum and palladium via an ethylene glycol reduction method. The synthesized Pt-Pd/C electrocatalyst later added with PBI and used as the ORR electrocatalyst in PEMFC was studied, along with the electrocatalyst activity and single cell performance. In this study, black Vulcan Carbon Xc-72 was employed as the support to deposited platinum and palladium via chemical reduction method. The synthesized Pt-Pd/C electrocatalyst later added with PBI and used as the ORR electrocatalyst in PEMFC in ultra-low metal loading (0.02 mg) was studied, along with the electrocatalyst activity and single cell performance.

1.2 Problem Statement and Hypothesis

The limited supply and high cost of the Pt used in PEMFC electrocatalysts necessitate a reduction in the Pt level. Generally, there are two ways to reduce the use of Pt in PEMFCs, that is; [1] Pt electrodes with low Pt content and [2] total or partial substitution of Pt with other metals. In the former case, as discussed in a

review (Wee *et al.*, 2007), the reduction of Pt loading in electrocatalysts can be achieved through an enhancement of the Pt utilization by increasing the active Pt sites, thinning the active layer thickness and introducing smaller, carbon-supported, nanometer-sized, Pt particles. Regarding the point (2), the partial or total substitution of platinum with palladium seems a promising way to reduce Pt content (Antolini, 2009). Pd, as other platinum-group metals, presents electrocatalytic activity for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR), but the HOR and ORR activities of Pd are considerably lower than those of Pt (Debe, 2012; Rau *et al.*, 2008; Salvador-Pascual *et al.*, 2007). The performance of Pd/C for the HOR as anode catalyst in PEMFC is very poor (Ham *et al.*, 2012). It has been found, however, that by addition of a very low amount, Pt assisted the HOR activity of Pd attains that of pure Pt (Zhu *et al.*, 2015; Zhang *et al.*, 2012). Indeed, many works showed that platinum addition increases the ORR activity of palladium and that the dependence of the ORR activity on the Pt content goes through a maximum. Moreover, the particle size of carbon supported metals increases going from Pt to Pt–Pd independently of the preparation method (He *et al.*, 2012). Not only that, Pt degradation and carbon corrosion on fuel cell operating in low temperature. A warmth condition of fuel cell could eliminate these phenomenon.

Recently, several researchers have used different polymers as ionomer binders in the catalyst layers for HT-PEMFC. From these studies, it was observed that when PTFE (Su *et al.*, 2013) and PVDF (Liang *et al.*, 2014), served as a binder and being introduced into the catalyst layer, the porosity is enhanced, and the transport of oxygen in the catalyst layer is facilitated due to the hydrophobic properties possessed by the polymer. Unfortunately, the effects of the different and optimum ratios between PBI ionomer binder and coupled catalyst, Pt-Pd/C on performance have not been investigated for HT-PEMFCs. Therefore, to take the challenge, the properties of Pt-Pd/C, synthesis as cathode electrocatalyst, can be modified with different PBI ionomer ratio and metal (Pt-Pd) loading at even higher temperature which probably could enhance the efficiency of the electrocatalyst.

It was hypothesized that the preparation of a uniform Pt-Pd distribution onto carbon support that having a coarser and high surface roughness will significantly increase the reaction site surface area for the ORR and allow delivered a promising power density for the fuel cell application at high operating temperature. Lastly, the introduction of the PBI ionomer to the catalyst layer will expected lead to a better oxygen transport and enhancement in electrocatalyst porosity.

1.3 Research Objectives

The objectives of this study are:

1. To synthesize a series of metal electrocatalysts supported onto carbon black and modified with PBI ionomer binder on the cathode catalyst layer
2. To study the physicochemical and electrochemical properties of the prepared electrocatalyst
3. To analyze the performance of the synthesized electrocatalyst on the single H₂/O₂ fuel cell at high operating temperature

1.4 Scope of Research

The scopes of this study consist of three parts which are the synthesis of all sample electrocatalysts, characterization of the samples and the potential of the coupled catalyst on the fuel cell. The details are described as below:

1. Synthesis of coupled electrocatalyst Pt-Pd supported onto carbon black and modified with PBI ionomer binder on the catalyst layer.
 - i. The Pt/C is synthesized in ethylene glycol via reduction method under ambient atmosphere at room temperature. The Pd is also supported on Pt/C to give Pt-Pd/C electrocatalyst in 10-40wt% metal loading using impregnation method. Preparation of modified electrocatalyst, PBI: Pt-Pd/C in different ratio is also conducted via the same method. The PBI solution was initially prepared by using DMAc. Pd/C and Pt/C were also being prepared as for reference electrocatalyst.

2. Characterization of the electrocatalyst
 - i. The physicochemical properties of the electrocatalyst were determined by different means of characterization. The specific electrochemically surface areas were investigated by cyclic voltammetry (CV) analysis which the values were then validated by the linear sweep voltammetry (LSV) analysis. LSV were also revealed E_{onset} and $E_{1/2}$ values for the coupled sample. The morphological properties and distribution metal onto supportive material were examined using field emission scanning electron microscope (FESEM) and energy dispersion X-Ray mapping (EDX-mapping) analysis. Nitrogen adsorption-desorption isotherms (Brunnauer-Emmett-Teller, BET) was used to obtain the textural properties of the electrocatalyst. The structural orientation, $d_{spacing}$ and wall thickness values of the prepared coupled electrocatalyst were recorded using X-ray diffraction (XRD) analysis. Fourier Transform Infrared Spectroscopy (FTIR) was conducted to identify functional group present in the prepared electrocatalyst. Short-term durability test for different period of

time were conducted to explore the stability of each modified sample.

3. The potential of the electrocatalyst were tested on the single fuel cell
 - i. Electrodes with different metal loading electrocatalyst were used to prepare the MEAs for PEMFC single cell performance tests. The screening process is conducted to determine the optimum condition including the effect of metal loading and effect of binder (PBI) in catalyst layer. The effect of metal loading was studied by preparing a series of weight loading onto carbon black supported (10, 20, 30 and 40 wt% Pt-Pd/C). Whereas, the effect of binder was investigated using a potential coupled catalyst by introducing the PBI onto it in a series of ratio (1: 99, 3: 97, 5:95 and 7: 93). The potential of best coupled and modified electrocatalyst were also studied at high operating temperature (170°C) in single H₂/O₂ fuel cell.

1.5 Significance of study

This study was conducted to synthesize coupled electrocatalyst (Pt-Pd/C). A detail investigation of catalyst properties as well as the performance on the fuel cell was conducted. It was known that platinum catalyst gain much attention for application on PEMFC despite its disadvantages which is costly and tend to degrade on temperature less than 80°C. However, the exploration towards this type of fuel cell becomes stagnant for past few years. Therefore, steps should be taken to develop a promising study that will counter both technology and environmental aspects. Thus, the introduction of different weight loading of Pt-Pd coupled catalyst and modification of coupled electrocatalyst layer with PBI ionomer offer an alternative way to produce a good electrocatalyst that could assist ORR which could enhance the

power density produce from fuel cell application. In addition, the findings and discussion from this study could be a capable alternative electrocatalyst in term of the improvement of new electrocatalyst for PEMFC at high operating temperature range. This study will optimistically provide a new insight to the research and science community.

1.6 Thesis Outline

This thesis is divided into five chapters. In Chapter 1, an introduction is given about the use of fossil fuels as dependence source energy and fuel cell as the new alternative energy production system. Among all type of fuel cell, PEMFC received much attention and has been selected to further explore. Recent studies regarding PEMFC and its drawback were also mentioned. The general introduction about the costly of the PEMFC due to the use of Pt as the conventional electrocatalyst was highlighted. The problem statement of the current research was stated to provide clear objectives of the present study with the scopes of study covers the research work that will be conducted to meet these objectives. In Chapter 2, the literature related to this study was reviewed. The overview on previous studies about conventional electroacatalyst, modification of PEMFC with polymer used as ionomer binder and high operating temperature had been explored. The synthesis methods on this study and characterization techniques also included.

The research design and methodology used in this studied was explained in Chapter 3. The materials and chemicals, catalyst preparation and characterization were described in this chapter. In Chapter 4, results and discussion was divided by synthesis and characterization followed by the H_2/O_2 fuel cell performance evaluations. All the results and proposed mechanisms were presented and discussed comprehensively. Finally, Chapter 5 covered the conclusions about the study. The recommendations for future studies were also given in this chapter.

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