Electrochemical synthesis of high active palladium-based catalysts for fuel cell

Poon, Kee Chun

2017

Poon, K. C. (2017). Electrochemical synthesis of high active palladium-based catalysts for fuel cell. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/72762>

<https://doi.org/10.32657/10356/72762>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**ELECTROCHEMICAL SYNTHESIS OF HIGHLY
ACTIVE PALLADIUM-BASED CATALYSTS FOR
FUEL CELL**

POON KEE CHUN

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2017

ELECTROCHEMICAL SYNTHESIS OF HIGHLY ACTIVE PALLADIUM-BASED CATALYSTS FOR FUEL CELL

POON KEE CHUN

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Acknowledgement

The author would like to take this opportunity to express his highest appreciation and gratitude to Asst. Prof. Hirotaka Sato, the author's supervisor for all his dedication, wisdom and guidance in helping the author throughout the project.

Next, the author would also like to thank Assoc. Prof. Su Haibin and Assoc. Prof. Richard D. Webster for their inputs and suggestion in helping the author in this thesis.

Next, the author would also like to appreciate Ms. Koh Joo Luang, Ms. Heng Chee Hoon, Ms. Yong Mei Yoke and Mr. Leong Kwok Phui at Material/Biological & Chemical Laboratories for their tireless support and help.

Lastly, the author would like to those who were not mentioned here but helped the author during this project.

Abstract

This thesis presents a facile and simple stepwise electroless deposition method for the synthesis of palladium nanoparticles for fuel cell application. The palladium nanoparticles synthesized by the proposed method exhibited high specific and mass activity for both oxygen reduction reaction and formic acid oxidation compared to commercial platinum and palladium loaded carbon. In particular, the amorphous palladium-phosphorus nanoparticles exhibited the highest specific and mass activity reported in literature so far. For oxygen reduction reaction, the palladium-phosphorus nanoparticles had a specific and mass activity of 6.85 mA cm^{-2} and $2.21 \text{ mA } \mu\text{g}^{-1}$ respectively which were 4.5 and 2.6 times greater than previously reported values. Furthermore for formic acid oxidation, the palladium-phosphorus nanoparticles had a specific and mass activity of 5.7 mA cm^{-2} and $2.9 \text{ mA } \mu\text{g}^{-1}$ respectively which were also higher than any previously reported literature values. The palladium nanoparticles were also shown to be more durable than commercial platinum and palladium loaded carbon. Furthermore, the palladium nanoparticles synthesized by the proposed method were also demonstrated to be industrial applicable. Lastly, the proposed synthesis method was also implemented in coating carbon nanotubes with palladium nanoparticles to make a palladium nanoparticles-carbon nanotubes composite. This palladium nanoparticles-carbon nanotubes composite was shown to be able to increase the catalytic and mass activity of bilirubin oxidase in oxygen reduction reaction compared to carbon nanotubes alone. Furthermore, this palladium nanoparticles-carbon nanotubes composite was also demonstrated to be able to increase the electron transfer rate between the bilirubin oxidase and the electrode (99.2 s^{-1} to 169.4 s^{-1}).

Table of Content

Acknowledgement	i
Abstract.....	ii
List of Figures	4
List of Tables	6
Abbreviation and Symbol List	7
1. Introduction.....	8
1.1 Background and Motivation.....	8
1.1.1 Fuel Cell	8
1.1.2 Bio-fuel Cell	9
1.2 Limitations	11
1.2.1 Limitations of Fuel Cell.....	11
1.2.2 Limitations of Bio-fuel Cell	11
1.3 Aims and Objectives	13
1.4 Scope	14
1.5 Organization of Thesis	15
2. Literature Review.....	16
2.1 Electrochemistry.....	16
2.2 Types of Fuel Cells	18
2.2.1 Proton Exchange Membrane Fuel Cell.....	18
2.2.2 Alkaline Fuel Cell.....	20
2.3 Bio-fuel Cell.....	21
2.4 Oxygen Reduction Reaction.....	22
2.5 Formic Acid Oxidation.....	23
2.6 Electrocatalysts.....	25
2.7 Comparison between Electrocatalysts for Oxygen Reduction Reaction in Alkaline Fuel Cell	26
2.7.1 Comparison between Onset Potentials	27
2.7.2 Comparison of Observed Current Densities at Specific Potential.....	27
2.8 Comparison between Electrocatalysts for Formic Acid Oxidation.....	31
2.9 Platinum / Platinum Nanoparticles.....	32
2.10 Palladium / Palladium Nanoparticles	34

2.10.1 Synthesis of Palladium Nanoparticles	34
2.10.2 Manipulating Size of Palladium Nanoparticles	35
2.10.3 Manipulating Shape of Palladium Nanoparticles	35
2.10.4 Formation of Bimetallic Palladium Nanoparticles	36
2.10.5 Using various support materials with Pd NPs	36
2.10.6 Manipulating Morphology of Pd NPs	37
2.11 Bilirubin Oxidase	38
3. Experimental Procedure	40
3.1 Stock Solution Preparation	40
3.2 Stepwise Electroless Deposition of Palladium Nanoparticles	42
3.3 Preparation of Platinum and Palladium loaded Carbon	43
3.4 Preparation of Bilirubin Oxidase Biocathode	43
3.5 Linear Sweep Voltammetry for Oxygen Reduction Reaction	43
3.6 Cyclic Voltammetry for Formic Acid Oxidation	44
3.7 Cyclic Voltammetry for Electrochemically Active Surface Area Measurement	45
3.8 Preparation of Inductively Coupled Plasma-Mass Spectrometry	45
3.9 Transmission Electron Microscopy / Scanning Transmission Electron Microscopy preparation	45
3.10 Scanning Electron Microscopy preparation	46
3.11 Preparation of X-ray Diffraction Samples	47
3.12 Preparation for Ultra Violet-Visible Light Spectroscopy	47
4. Results and Discussions for Oxygen Reduction Reaction	48
4.1 Synthesizing the Palladium Nanoparticles	48
4.2 Characterizing the Palladium Nanoparticles	50
4.3 Oxygen Reduction Reaction Polarization Curves of Palladium Nanoparticles	52
4.4 Calculation and Analysis of the Specific Activity of Palladium Nanoparticles in Oxygen Reduction Reaction	55
4.5 Calculation and Analysis of the Mass Activity of Palladium Nanoparticles in Oxygen Reduction Reaction	64
4.6 Importance of Amorphous Nature and Industrial Application of Palladium Nanoparticles in Oxygen Reduction Reaction	67
4.7 Durability Test for Palladium Nanoparticles in Oxygen Reduction Reaction	70
5. Results and Discussion for Formic Acid Oxidation	72
5.1 Cyclic Voltammetry Curves for Formic Acid Oxidation	72

5.2 Calculation and Analysis of the Specific and Mass Activity of Palladium Nanoparticles for Formic Acid Oxidation.....	75
5.3 Importance of Amorphous Nature of Palladium Nanoparticles in Formic Acid Oxidation.....	81
5.4 Durability Test of the Palladium Nanoparticles for Formic Acid Oxidation	82
6. Results and Discussions for Bio-Fuel Cell	83
6.1 Synthesis of Carbon Nanotubes-Palladium Nanoparticles Composite by Stepwise Electroless Deposition	83
6.2 Characterization of Carbon Nanotubes-Palladium Nanoparticles Composite	85
6.3 Cyclic Voltammetry of Bilirubin Oxidase with Carbon Nanotube-Palladium Nanoparticles Composite as Support Material.....	87
6.4 Importance of Palladium Nanoparticles in Enhancing Oxygen Reduction Reaction for Bilirubin Oxidase	90
7. Conclusion and Future Work	91
7.1 Conclusion.....	91
7.2 Future Work	94
List of Publication.....	97
References.....	98

List of Figures

Figure 1. Diagram of a typical fuel cell.	9
Figure 2. Diagram of PEMFC.....	19
Figure 3. Diagram of AFC	20
Figure 4. Diagram of BFC	22
Figure 5. FAO reaction pathway.....	24
Figure 6. FAO curve of (a) Cu/Pd porous structure and (b) Cu/Pd film structure	25
Figure 7. Crystal structure of BOD (Myrothecium Verrucaria)	39
Figure 8. TEM, ED and EDS of Pd-P and Pd-N ₂ H ₄	51
Figure 9. XRD of Pd-P and Pd-N ₂ H ₄	51
Figure 10. ORR polarization curves for different deposition cycles of Pd-P and Pd-N ₂ H ₄ at 1600 rpm.....	54
Figure 11. ORR polarization curves for different deposition cycles of Pd-P and Pd-N ₂ H ₄ at 400, 900, 1600 and 2500 rpm.....	57
Figure 12. K-L plot for different deposition cycles of Pd-P and Pd-N ₂ H ₄	58
Figure 13. Full CV of 9 cycles Pd-P in N ₂ -saturated 0.1 M KOH solution.....	59
Figure 14. Full CV of Pt/C s in N ₂ -saturated 0.1 M KOH solution.....	60
Figure 15. Full CV of different deposition cycles of Pd-P and Pd-N ₂ H ₄ in N ₂ -saturated 0.1 M KOH solution	61
Figure 16. ORR polarization curve of blank GC-RDE and 9 cycles Pd-P in O ₂ -saturated 0.1 M KOH solution before and after HNO ₃ extraction.....	65
Figure 17. ORR polarization curves of 9 cycles Pd nanoparticles synthesized on carbon cloth before and after annealing.....	69
Figure 18. EDS of 9 cycles Pd-P after annealing at 700 °c for 1 hour.....	69
Figure 19. Chronoamperometry response of Pd NPs, Pt/C and Pd/C at 200 rpm..	71

Figure 20. CV curves for amorphous Pd-P NPs for FAO.....	72
Figure 21. Full CV of different deposition cycles of Pd-P in N ₂ -saturated 0.5 M H ₂ SO ₄ + 0.1 M HCOOH.....	78
Figure 22. SEM images of different deposition of Pd-P with their size distribution....	79
Figure 23. Forward scan curves for Pd-P NPs for FAO normalized by (a) ECSA to give specific activity and (b) Pd loading to give mass activity.....	80
Figure 24. Specific activity graphs for FAO of 6 cycles Pd-P NPs deposited on carbon cloth before and after annealing.....	81
Figure 25. Chronoamperometry results for both 9 cycles Pd-P and Pd/C for FAO.	82
Figure 26. 9 cycles CNT-Pd composite viewed under (a) SEM, (b) STEM, (c) TEM and (d) particle size distribution graph.	86
Figure 27. ORR polarization curves of CNT-BOD and CNT-Pd-BOD with (a) full CV and (b) zoomed in potential range and mass activity curve.....	88
Figure 28. UV-Vis curves of (a) different amounts of BOD for calibration and (b) CNT-BOD and CNT-Pd-BOD. (c) shows the calibration plot obtained from (a) at 420 nm.	89

List of Tables

Table 1. Thermodynamic electrode potential for O ₂ reduction	23
Table 2. Standard values for constants used ^[40]	28
Table 3. Summary of concentration of chemicals used for different experiments.	42
Table 4. Half-wave potential values of Pd and Pt obtained from Figure 9.....	54
Table 5. Number of electrons transferred and specific activity values of Pd and Pt	63
Table 6. Mass activity values of Pd and Pt electrocatalysts	66
Table 7. Specific, Mass Activities and average P content values for Pd-P and Pd/C at peak potential	80
Table 8. Computational calculation of adsorption energies and distance between Cu active sites and substrate.	84

Abbreviation and Symbol List

Abbreviation	Description
ORR	Oxygen Reduction Reaction
FAO	Formic Acid Oxidation
PEMFC	Proton Exchange Membrane Fuel Cell
DFAFC	Direct Formic Acid Fuel Cell
BFC	Bio-fuel Cell
Pt	Platinum
Pd	Palladium
Pt/C	Platinum loaded carbon
Pd/C	Palladium loaded carbon
BOD	Bilirubin Oxidase
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
UV-Vis	Ultra Violet - Visible Light Spectroscopy
EDS	Energy-dispersive X-ray Spectroscopy
XRD	X-ray Diffraction
AFC	Alkaline Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
MCFC	Molten Carbonate Fuel Cell
SOFC	Solid Oxide Fuel Cell
HOR	Hydrogen Oxidation Reaction
H₂O₂	Hydrogen Peroxide
i_k (mA)	Kinetic Current
i_d (mA)	Diffusion Limit Current
i_s (mA cm⁻²)	Kinetic Current Normalized by ECSA
i_m (mA μg⁻¹)	Kinetic Current Normalized by catalyst load
K-L plot	Koutecky-Levich Plot
ECSA	Electrochemically Active Surface Area
Pt NPs	Platinum Nanoparticles
Pd NPs	Palladium Nanoparticles
NaH₂PO₂	Sodium Hypophosphite Monohydrate
N₂H₄	Hydrazine Hydrate
PdCl₂	Palladium Chloride
Pd-P	Palladium nanoparticles synthesized with NaH ₂ PO ₂
Pd-N₂H₄	Palladium nanoparticles synthesized with N ₂ H ₄
LSV	Linear Sweep Voltammetry
CV	Cyclic Voltammetry
RDE-GC	Rotating Disc Electrode - Glassy Carbon
J (mA cm⁻²)	Current density
E (V)	Potential
Pd N₂H₄-CNT	Palladium Nanoparticles-Carbon Nanotubes Composite

1. Introduction

1.1 Background and Motivation

1.1.1 Fuel Cell

With the increasing demand for power and the rapid depletion of fossil fuels, fuel cell has been gaining popularity due to its nature as a renewable source of energy.^[2] Basically, fuel cell works by converting chemical energy into electrical energy with the by product being heat and water. Among other sources of renewable energy (eg. photo voltaic and wind turbine), fuel cell has the highest energy efficiency as well as relatively low capital, operation and management cost.^[2-3] These factors has led to the significant increase in research interest of fuel cell in many countries such as USA, Japan and Canada.^[2]

Despite having many variations, fuel cells in general has 3 main parts: the anode, cathode and electrolyte as shown in Figure 1.^[4] Each of these parts play an important role ensuring that the fuel cell functions. Firstly at the anode, a catalyst converts the fuel (dependent on the type of fuel cell) into ions and electrons. The ions travel through the electrolyte and a membrane (which allows only ions not electrons to pass through) to the cathode. The electrons on the other hand travels through the wire, typically connected to a load, to the cathode. This process of the electron travelling from the anode to the cathode serve to drive the load. Finally at the cathode, another catalyst combines the ions and electrons back into water as its waste product. All in all, in a typical fuel cell, the fuel is consumed to produce an electric current which drives a load and by products in the form of water and heat.^[2, 5]

Figure 1. Diagram of a typical fuel cell.

1.1.2 Bio-fuel Cell

Biological fuel cell or more commonly known as bio-fuel cell (BFC) is a subset of fuel cell which has gained prominence over the years as fuel cell has been establishing a solid foothold in the energy industry.^[6-7] The way that bio-fuel cell works is almost identical to that of traditional fuel cell which is the conversion of chemical energy into electrical energy. However, the main difference between bio-fuel cell and fuel cell is that bio-fuel cell relies typically on enzymes (eg. glucose oxidase and bilirubin oxidase) to act as the catalysts for the reaction (in at least one side of the electrode) and biomass (eg. glucose and trehalose) to act as a source of fuel.^[6-8]

The main application of bio-fuel cell is to be a sustainable and renewable source of power for implanted systems in living organisms. An example of such an application of bio-fuel cell is pacemakers where the bio-fuel cell replaces the battery as a power

source. This would hopefully eliminate the need of changing the pacemaker due to the expiration of the battery.^[6, 9]

As the aim of bio-fuel cell is to be implanted into living organisms, enzymes are used in place of traditional catalysts such as platinum (Pt). This is because enzymes are highly selectively and will only react with their specific substrate (eg. glucose oxidase and glucose).^[7, 10] This is in contrast to Pt which is more expensive, not as selective which may result in unintended side reactions when implanted and also low onset potentials at near neutral pH (operating pH of bio-fuel cell).^[11] Furthermore, using these highly selective enzymes as catalysts, it can eliminate the need for an ionic conductive membrane and allows for mixture of reactant which in turn enables the miniaturization of the bio-fuel cell (no separation of cathode and anode).^[7] Due to these advantages, bio-fuel cell has seen a surge in popularity in both medical and energy industries.^[6, 12]

1.2 Limitations

Although both fuel cell and bio-fuel cell have numerous advantages, they are not without their shortcomings. In both cases, they share a similar disadvantage in that they require an electrocatalyst to increase the rate of reaction at both the cathode and anode. These disadvantages and other drawbacks are described in greater detail below.

1.2.1 Limitations of Fuel Cell

As mentioned above, regardless of the types of fuel cell (acid, alkaline or bio-fuel cell), there is a need for electrocatalyst to increase the rate of reaction at both the cathode and anode because despite the reactions are both sides being thermodynamically favoured, they are kinetically slow.^[2, 13-14]

At the cathode, the key reaction that takes place is oxygen reduction reaction (ORR) while at the anode many different reactions may take place and is highly dependent on the type of fuel cell and the electrolyte being used. For fuel cells in general, currently the best electrocatalysts for both reactions is Pt.^[2, 13]

Although Pt is currently the best electrocatalyst due to its high catalytic activity, it is not without flaws. Pt is an expensive metal and is a non-renewable resource.^[2, 13, 15] Furthermore, Pt is known to have poor durability due to its susceptibility of being poisoned by the electrolyte itself.^[13, 15] Also, the preparation of Pt electrocatalyst requires complicated handling procedures and harsh conditions (eg. high temperature) which severely limits its applications.^[16-18] Therefore, there is a need to find a cheaper and more durable alternative.

1.2.2 Limitations of Bio-fuel Cell

As previously mentioned, bio-fuel cell requires electrocatalysts to speed up the rate of reaction as well. At the cathode where ORR takes place, one of the more commonly

used enzyme is bilirubin oxidase (BOD) while at the anode, the enzyme most frequently used is glucose oxidase (GOD) with the biomass (fuel) used being glucose.^[1, 19]

Unfortunately, these enzymes share some of the same shortcomings as their traditional metal counterparts. These include having tedious and difficult preparation procedures as well as poor durability.^[1, 6-7, 19] Furthermore, these enzymes also suffer from additional difficulties not seen in traditional metal electrocatalysts.

One such problem is the poor electron transfer between the enzyme and the electrode. Even though these enzymes have high selectivity, the active sites of these enzymes are located deep in their protein fold. Because of this, the electron has a difficult time travelling from the active side to the electrode or from the electrode to the active site (dependant on the reaction taking place).^[6-7] Although redox mediators have shown some benefits in solving this poor electron transfer problem, introducing such mediators results in other problems due to the reactive nature of these mediators.^[6-7]

Another problem with using enzymes is that the enzymes are highly conformation dependant. Due to the active site location being deep in the protein fold, the conformation of the enzymes on the supporting material (eg. carbon nanotubes (CNT)) needs to be specific in order for easy access of the reactant to the active sites of the enzymes. Furthermore, the conformation also affects the distance between electrode and active site which in turn also affects the electron transfer rates between the electrode and the active site.^[7, 20-21]

Therefore, there is a need to develop a support material which is able to both improve the electron transfer rate between electrode and enzyme as well

as enable the enzyme to bind to it in the enzyme's preferential conformation configuration.

1.3 Aims and Objectives

This thesis aims to develop a facile synthesis method to synthesize stable palladium nanoparticles (Pd NPs) electrocatalysts as an alternative to Pt. These Pd NPs will be characterized and their electrocatalytic performance in fuel cell will be evaluated. Furthermore, these Pd NPs will also be investigated as a suitable support material for bio-fuel cell. Therefore, the objectives are:

- To synthesize stable Pd NPs directly onto the electrode surface to simplify and quicken the old synthesis process;
- To achieve superior catalytic/specific/mass activity with comparison to commercial Pt loaded carbon (Pt/C) and Pd loaded carbon (Pd/C);
- To achieve better durability compared to commercial Pt/C, Pd/C;
- To deposit Pd NPs onto CNT using the facile synthesis method and use it as a suitable support material for bio-fuel cell.

1.4 Scope

In order to achieve the aims and objectives, the scope of the project are:

- To develop a simple yet facile method of synthesizing Pd NPs directly onto the electrode;
- To evaluate the Pd NPs catalytic/specific/mass activity with comparison to commercial Pt/C and Pd/C;
- To evaluate the Pd NPs durability compared to Pt/C and Pd/C;
- To test the potential of the facile synthesis method of Pd NPs in industrial application of fuel cell;
- To observe and explain any trends observed in the catalytic activity of Pd NPs;
- To evaluate the ability of Pd NPs on CNT as a suitable support for enzymes in bio-fuel cell.

1.5 Organization of Thesis

This thesis consists of 7 chapters. A brief description of each chapter is given below:

Chapter 1 gives the introduction, limitations, aims and objectives, scope and organization of this thesis.

Chapter 2 presents a comprehensive literature review about the research. The theory behind the choices of the electrocatalysts as well as the evaluation methods for the said electrocatalysts are explained.

Chapter 3 describes and explains the experimental designs and procedures.

Chapter 4 discusses and evaluates the results of the ORR experiments.

Chapter 5 contains the results and discussion of the formic acid oxidation (FAO) experiments.

Chapter 6 presents the preliminary results of Pd NPs on CNT as suitable support in BFC.

Chapter 7 gives the overall summary of this thesis. Suggestions for future work are also described here.

2. Literature Review

2.1 Electrochemistry

Electrochemistry is a branch of chemistry that studies the conversion between chemical and electrical energy.^[22] Hence, electrochemistry is the main backbone of fuel cell. Therefore, in order to understand and improve the electrocatalysts used in fuel cell there is a need to first understand electrochemistry. In general, there are two main reactions in electrochemistry which are electrochemical reaction and reduction-oxidation (redox) reaction.

In electrochemical reaction, an external source (electrical energy) is required to induce the chemical reaction. This is also commonly known as electrolysis. By passing an electric current through an ionic substance that is either molten or dissolved in a suitable solvent, chemical reactions takes place at the electrodes which involves the absorbing and releasing of electrons. This will typically cause the formation or separation of materials/products at the electrode depending on various factors such as type of solvent and electrode.^[23] A common example of electrolysis would be electroplating where metals are coated onto a substrate to change its surface properties.^[24]

On the other hand, in redox reaction, the chemical reaction itself will provide the electron transfer which in turn generates electricity. This process occurs when there is a change in oxidation state of the ion or molecule involved in the reaction. For oxidation, the molecule or ion loses one or more electron which would cause its oxidation state to increase. An example would be $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$. Whereas for reduction, the molecule or ion gains one more electron which causes its oxidation state to decrease. An example would be $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$.

For fuel cell, the main reaction behind the conversion from chemical to electrical energy is redox reaction. In a typical fuel cell set up, oxidation occurs at the anode which supplies the electron while reduction occurs at the anode which accepts the electron. The electron travels from the anode to the cathode through a wire, which is connected to a load, and this in turn drives the load. Overall, this is how a typical fuel cell works.^[2, 13, 25]

Hence, by understanding the types of reaction that takes places at both anode and cathode (oxidation and reduction respectively), this will allow for greater insight when selecting and synthesizing suitable electrocatalysts for each respective electrode. However, there are other factors such as the type of fuel cell which will also be an important factor in deciding a suitable electrocatalysts.

2.2 Types of Fuel Cells

As mentioned earlier, the type of fuel cell will influence the type of electrocatalysts used in both sides of the electrodes of the fuel cell. In general, fuel cells are identified by the type of electrolyte which it uses which can be broken down into five categories:^[5]

1. Proton Exchange Membrane Fuel Cell (PEMFC)
2. Alkaline Fuel Cell (AFC)
3. Phosphoric Acid Fuel Cell (PAFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Solid Oxide Fuel Cell (SOFC)

In this thesis, the focus will be on two types of fuel cells, mainly PEMFC and AFC. Both PEMFC and AFC are similar in many areas and have significant advantages over the other remaining 3 different types of fuel cells. These advantages include:^[2-3, 5]

- Low operating temperature (under 100 °C)
- High power density
- Compact system
- Ease in handling fuel

2.2.1 Proton Exchange Membrane Fuel Cell

In PEMFC, its unique design is in its semipermeable membrane.^[5] This membrane is special as it allows only hydrogen ions (protons) but not electrons (causing short circuit) or gas (gas crossover) to pass through as seen in Figure 2. One of the more commonly known material used to make this membrane is fluoropolymer Nafion (PFSA).^[26] At the anode of the PEMFC, hydrogen is supplied as the fuel. In a typically PEMFC, hydrogen oxidation reaction (HOR) occurs at the anode where the hydrogen

is oxidised to hydrogen ions and electrons as shown in Equation 1. The hydrogen ions permeate through the membrane to the cathode while the electrons travel through the external circuit load generating the current output of the fuel cell.^[27] At the cathode, the hydrogen ions react with oxygen gas and the electrons arriving from the external load to give water as shown in Equation 2. This is also known as oxygen reduction reaction (ORR).^[13]

Figure 2. Diagram of PEMFC

2.2.2 Alkaline Fuel Cell

AFC also shares the same unique design in that it uses a semipermeable membrane as well. However, the main difference is that the membrane that AFC uses only allows hydroxide ions (anions) and not electrons or gas to pass through as shown in Figure 3.^[13, 25, 28] A commonly used membrane in AFC is poly(ethylene-co-tetrafluoroethylene) (ETFE).^[25] The reactions at the electrodes are also slightly different in AFC. In a typical AFC anode, HOR occurs with hydrogen reacting with hydroxide ions to form water and electrons as seen in Equation 3. On the other hand, at the cathode, ORR also takes place with oxygen, water and electrons (arriving through the wire from the anode) reacting to give hydroxide ions as observed in Equation 4.^[25]

Figure 3. Diagram of AFC

2.3 Bio-fuel Cell

Bio-fuel cell (BFC), as reported earlier is a subset of fuel cell. It has the same basic setup as fuel cell with a cathode, anode as well as electrolyte. Also mentioned earlier is that the main difference between BFC and fuel cell is that BFC uses biomass as the source of fuel and that the electrocatalysts used are typically enzymes as seen in Figure 4.^[1]

At the anode of a typical BFC setup, the reaction is complicated and would depend heavily on the type of biomass used as a source of fuel. In a traditional BFC, glucose is one of the most frequently used biomass. In order to oxidise glucose, the enzyme glucose oxidase (GOD) is commonly used. GOD oxidises the glucose into gluconolactone, hydrogen ions and electrons as shown in Equation 5.^[1, 19, 29] The electrons from this reaction will travel through the wire, driving the load, before arriving at the cathode. At the cathode, ORR is still the main reaction that occurs for BFC as seen in Equation 6. One of the most commonly used bio-cathodic enzyme electrocatalyst is bilirubin oxidase (BOD). BOD works by accepting electron from the anode and catalysing oxygen into water.^[1, 19, 21] This overall setup for the BFC is summarised in Figure 4.

Figure 4. Diagram of BFC

2.4 Oxygen Reduction Reaction

As mentioned before, ORR is the key reaction that occurs in the cathode for PEMFC, AFC and BFC. In aqueous solution, ORR occurs mainly through two pathways, four electron reduction pathway (from O_2 to H_2O) or two electron reduction pathway (from O_2 to H_2O_2) as shown in Table 1. However, in non-aqueous aprotic solvents, one electron reduction pathway can also occur (from O_2 to O_2^-).

The four electron reduction pathway is the preferred over the two electron reduction pathway as it is more efficient (four electron transfer compared to two electron transfer). Furthermore, four electron reduction pathway forms water as the product whereas two electron reduction pathway gives toxic hydrogen peroxide (H_2O_2) as the product. However two electron reduction pathway is still sometimes preferred especially in industries that manufacture H_2O_2 .^[13]

Table 1. Thermodynamic electrode potential for O₂ reduction

Electrolyte	ORR	Thermodynamic Electrode Potential at Standard Conditions, V
Acid Aqueous Solution	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$	1.229
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Alkaline Aqueous Solution	$O_2 + H_2O + 4e^- \rightarrow 4OH^-$	0.401
	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.867

2.5 Formic Acid Oxidation

In PEMFC, the reaction that occurs at the anode depends largely on the type of fuel as well as the electrolyte used. In this thesis, the focus will be on direct formic acid fuel cell (DFAFC) which is a subcategory of PEMFC.

In DFAFC, formic acid oxidation (FAO) occurs at the anode. In FAO, formic acid which is the fuel used, is oxidized to give carbon dioxide, hydrogen ions and electrons as shown in Figure 5.

As shown in Figure 5, FAO can proceed by either one or both of the pathway. However, the dehydrogenation pathway is the preferred over the dehydration pathway. This is because dehydrogenation pathway oxidizes the formic acid directly to carbon dioxide and avoids the formation of carbon monoxide (CO_{ads}) intermediate which poisons the catalysts.^[30]

As seen in Figure 6, the two reaction pathway can be allocated to two different peaks in the forward scan of the FAO curve. The peak shown between 0 V to 0.3 V is associated with the dehydrogenation pathway while the peak at 0.45 V is allocated to the dehydration pathway.^[31] Hence, a large peak at 0 V to 0.3 V is preferred while the peak at 0.45 V is undesired.

Figure 5. FAO reaction pathway

Figure 6. FAO curve of (a) Cu/Pd porous structure and (b) Cu/Pd film structure in N_2 -saturated 0.5 M H_2SO_4 + 1 M $HCOOH$ solution. Scan rate: 50 mV s^{-1} ^[31]

2.6 Electrocatalysts

Electrocatalysts as stated earlier are catalysts which are used in electrochemical reaction to speed up the rate of reaction. They are usually used to increase the rate of the reaction without being consumed in the process.

For ORR, even though it is thermodynamically favoured, the process itself is kinetically slow. This slow kinetics is mainly due to the need to break the strong oxygen double bond (498 kJ mol^{-1}) during the ORR process.^[14] Hence there is a need for an electrocatalyst to lower the activation energy and increase the rate of reaction of the ORR.

There are 3 common methods in which the effectiveness of electrocatalysts can be evaluated. One of these methods is using the Tafel equation. Tafel equation is shown in Equation 7:

$$\eta = \frac{RT}{\alpha F} \ln i_o - \frac{RT}{\alpha F} \ln i \quad (7)$$

where η is the overpotential (V), i_o (mA) is the exchange current, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the universal gas constant, T (K) is the temperature, α is the charge transfer coefficient and F (C mol^{-1}) is the Farady's constant. By using the Tafel equation to plot a Tafel plot, the exchange current can be extrapolated. This exchange current can be described as current passing through the electrode at equilibrium. Therefore electrocatalyst aims to increase the exchange current which would in turn increase the current at all overpotential where the observed current is supposed to be kinetically limited. However, this method of comparison is not effective as the exchange current is magnitudes smaller than the observed current. Furthermore, the extrapolation of exchange current from the Tafel plot is an estimated value and would result in large uncertainties. ^[17, 32] Therefore, the other 2 methods which are onset potentials and specific and mass activities are used for comparison instead and are described in greater details in the following section of this Chapter.

2.7 Comparison between Electrocatalysts for Oxygen Reduction Reaction in Alkaline Fuel Cell

As mentioned earlier, there are two other methods of evaluating the efficiency between the electrocatalysts:

1. Comparison of onset potentials between the electrocatalysts,^[33-34]
2. Comparison of the observed current densities at specific potential:^[17, 35-36]
 - a. Comparison using mass activity;
 - b. Comparison using specific activity.

2.7.1 Comparison between Onset Potentials

One of the methods of comparing the efficiency of different electrocatalysts is through the comparison of their onset potentials. This is achieved by observing the potential at which the start of the ORR occurs which would be indicated by the increased observed current density with respect to open circuit potential. Hence, the more positive the onset potential is, the better the electrocatalyst.^[33-34]

A variation to this method would be to calculate the half-wave potentials between the electrocatalysts. In this method, the limiting current density is first observed from the ORR polarization curve. Next, the current density is halved and the corresponding potential is noted. This variation is more accurate as the onset potential takes into consideration the limiting current density achieved. Again, the more positive this potential value is, the more active the electrocatalyst is.^[37-38]

However, this comparison using the onset potential is only effective in quantitatively evaluating the effectiveness of the catalysts. This is because this method is rather imprecise as it does not take into consideration the amount of catalyst which is loaded onto the electrode surface.

2.7.2 Comparison of Observed Current Densities at Specific Potential

In this method of comparison, the current densities of the electrocatalysts are compared with each other at specific potential (0.85 V vs RHE). This potential is selected with reference to the previous literature reported.^[35] Whichever electrocatalysts has the higher current density at that potential would be the superior electrocatalyst. Nevertheless, this comparison is only possible if the current used in the comparison is kinetically controlled. Hence, there is a need to determine the actual

current density (kinetic current) value using the Koutecky-Levich Equation^[35, 39-40]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (8)$$

which can be further expanded as such:

$$\frac{1}{i_d} = \frac{1}{B\omega^{\frac{1}{2}}} \quad (9)$$

$$B = 0.62nFS c_o D^{\frac{2}{3}} \nu^{-\frac{1}{6}} \quad (10)$$

where i (mA) is the current measured at the mixed diffusion-kinetics control region, i_k is the kinetic current to be calculated, i_d (mA) is the diffusion limit current (current that is diffusion controlled) measured from experiment, B is the Levich constant, ω (rad s⁻¹) is the rotational speed of the electrode, n is the number of electrons transferred per O₂ molecule, F (C mol⁻¹) is the Faraday's constant, S (cm²) is the electrode surface area, c_o (mol cm⁻³) is the concentration of dissolved O₂ in the solution, D (cm² s⁻¹) is the diffusion coefficient of the dissolved O₂ and ν (cm² s⁻¹) is the kinematic viscosity of the solution. The standard values for the constants used in this calculation is listed below in Table 2.

Table 2. Standard values for constants used^[40]

Constant	Value
F	96485 C mol ⁻¹
S	0.0707 cm ²
C_o	1.2 x 10 ⁻⁶ mol cm ⁻³
D	1.9 x 10 ⁻⁵ cm ² s ⁻¹
ν	0.01 cm ² s ⁻¹

Based on the Koutecky-Levich Equation, the i_k value can be obtained. With the i_k value, comparison between the effectiveness of the electrocatalysts can be made. However, this i_k value does not take into consideration the amount of electrocatalyst

which is loaded onto the electrode. Hence, it might give inaccurate results as a large amount of Catalyst A might give a higher i_k value compared Catalyst B but in actual fact Catalyst B is the more effective catalyst when the same amount of catalyst is used. Hence a more in-depth calculations is needed to give more accurate evaluation of the catalysts. This would be mass and specific activity calculations.

2.7.2a Comparison by Mass Activity

With the kinetic current value obtained from the Koutecky-Levich equation, a more accurate evaluation method would be to take into consideration the mass activity of the electrocatalysts. In other words, this would effectively take into account the amount of electrocatalysts which is loaded onto the electrode surface and hence obtain a precise representation of the efficiency of the electrocatalysts.

In the mass activity calculation, the i_k value is simply normalized with the amount of electrocatalysts loaded on the electrode.^[17, 35-36] This would give the cost effectiveness of the electrocatalyst as it shows the amount of current generated for each gram of electrocatalyst loaded onto it. An alternative calculation can also be made which is specific activity calculations.

2.7.2b Comparison by Specific Activity

In specific activity calculations, the efficiency of the electrocatalyst is evaluated based on electrochemically active surface area (ECSA). This is because catalysts in general only have certain facets which are actually used in the catalysis process. Hence, by normalizing the i_k value with the ECSA, the comparison can be made between the electrocatalysts with respect to the amount of active surface area that the catalyst has.

Furthermore, by normalizing with ECSA, factors such as particle size and dispersion of the NPs are taken into account as well. ^[35, 37, 41] Also, this would be useful in comparing electrocatalysts that have similar mass activities.

As mentioned previously, not all facet of the electrocatalysts is used in the catalysis process. Only certain facets of the electrocatalysts are favourable for the attachment of oxygen for ORR. ^[17, 36, 42] Hence, the ECSA of these electrocatalysts need to be calculated. In general, in the calculation of the ECSA, the charge of the electrocatalysts (eg. PdO reduction to Pd) is compared to that of its standard charge value which was obtained under standard condition (eg. PdO reduction charge is $405 \mu\text{C cm}^{-2}$). ^[35, 43] In order to obtain this charge, the full cyclic voltammetry (CV) of the electrocatalyst needs to be obtained. An example would be the full CV of palladium (Pd) obtained in N₂-saturated solution to avoid the charge contribution of ORR. From the full CV, the charge of the electrocatalyst can be estimated using integration as well as the scan rate of the CV. With the charge value, the ECSA value can be easily calculated with the standard value from literature.

2.8 Comparison between Electrocatalysts for Formic Acid Oxidation

For the comparison of the electrocatalysts for FAO, the method is slightly different to that of ORR. In FAO, a full CV scan without rotation is usually conducted for both the FAO as well as ECSA calculations. Hence, without different rotation speed, the Koutecky-Levich equation cannot be used and the i_k cannot be obtained. Therefore, for FAO, the current obtained from the full CV is simply normalized by the ECSA or by the amount of Pd loaded to obtain the specific and mass activity value and these values are used to compare different electrocatalysts.^[31, 44-45]

In the case of ECSA, there is only a slight difference in calculations between ORR and FAO which is the value for the reduction of PdO monolayer is slightly different (405 $\mu\text{C cm}^{-2}$ for ORR and 424 $\mu\text{C cm}^{-2}$ for FAO).^[31]

2.9 Platinum / Platinum Nanoparticles

Platinum (Pt) is Group 10 metal on the periodic table and also one of the rarest metals in the Earth's crust with an average abundance of $5 \mu\text{g kg}^{-1}$.^[46] It is often considered a noble metal due to its high corrosive resistance and generally unreactive nature. It is also used most commonly as catalysts as well as jewellery, drugs and electrodes.^[47] However, due to it being rare, the cost of Pt is usually very high and hence cheaper alternatives are preferred.

As mentioned before, one of the most common use of Pt is as a catalyst in chemical reactions. It is frequently used in catalytic converters in cars^[48] (eg. Pt black) and also in hydrogenation of unsaturated hydrocarbons^[49] (eg. PtO_2). This wide spread use of Pt is also seen very often in fuel cell, especially ORR. To this date, Pt (and its variant platinum nanoparticles (Pt NPs)) is still the best and most widely used catalyst for both ORR and FAO despite its high costs.^[13, 16-18] The typical specific and mass activity for Pt/C in ORR is 0.21 mA cm^{-2} and $0.89 \text{ mA } \mu\text{g}^{-1}$ while in FAO it is 0.08 mA cm^{-2} and $0.025 \text{ mA } \mu\text{g}^{-1}$.^[50-51] Cheaper substitutes has been the focus of many researchers in the electrochemistry field. Such cheaper alternatives include reducing the amount of Pt used by introducing various support materials (Pt/C, Pt black) and even using Pt alloys (PtPd, PtCu) to give bimetallic compounds.^[15, 35-36, 41, 52-53]

The high cost of Pt is not the only shortcoming for using it as an electrocatalysts for ORR and FAO. Another problem associated with Pt is its poor durability. This means that although Pt might give high initial current output, this output drops significantly over extended periods of time. Furthermore Pt electrocatalyst is highly susceptible to poisoning from the electrolyte itself which poses another problem.^[13, 54-55]

Hence, a superior alternative would be to use a material which is cheaper, able to exhibit similar catalytic properties to that of Pt and have improved durability compared to Pt.

2.10 Palladium / Palladium Nanoparticles

Palladium (Pd) is also a Group 10 metal and is relatively similar to Pt in many properties. It is also classified as a noble metal due to its inert nature. Therefore it is not surprising that the uses of Pd often overlap with that of Pt such as usage in catalytic converters as well as dentistry.^[56] Even though Pd is not cheap, based on market study over the past decade, Pt has always cost more than Pd with the price of Pt at one point being 5.5 times more expensive than Pd.^[57] Furthermore, not only is the catalytic activity of Pd is comparable to that of Pt especially in ORR and FAO, the durability has shown to be significant better as well.^[35, 58-60] The highest specific and mass activity reported for Pd is 1.52 mA cm^{-2} and $0.84 \text{ mA } \mu\text{g}^{-1}$ for ORR and 0.3 mA cm^{-2} and $0.005 \text{ mA } \mu\text{g}^{-1}$.^[31, 35] Therefore this thesis has decided to use Pd (in the form of palladium nanoparticles (Pd NPs)) as a suitable replacement for Pt.

Furthermore, recent studies on Pd as an electrocatalysts has shown many unique advancements. These advancements include:

1. Synthesis of Pd NPs;^[61]
2. Manipulating size of Pd NPs;^[58]
3. Manipulating shape of Pd NPs;^[62]
4. Formation of bimetallic Pd NPs;^[63-64]
5. Using various support materials to improve Pd NPs catalytic activity;^[35, 52]
6. Manipulating morphology of Pd.^[65-66]

2.10.1 Synthesis of Palladium Nanoparticles

Although Pd has seen increasing popularity as a replacement for Pt, there are still hurdles to overcome in the form of the synthesis of Pd NPs. In the traditional synthesis

and application of Pd NPs for fuel cell use, it typically requires harsh conditions such as high temperature (eg. heating up to 300 °C) and long and complicated handling procedures (eg. 6 hours required for preparation of carbon paste for coating of carbon paper for fuel cell application).^[35, 61] Recently, there has been advancements in trying to simplify and shorten the entire process by using a one pot synthesis method for synthesizing the Pd NPs.^[61] However, there are still further improvements that can be made and this thesis will attempt to further simplify the entire process to include the deposition of the Pd NPs onto the electrode material itself.

2.10.2 Manipulating Size of Palladium Nanoparticles

It has been reported that size of the Pd NPs greatly affects the catalytic activity of the Pd NPs.^[58] The trend observed is that the catalytic, specific and mass activity of Pd NPs increases with increasing particle size (diameter). This trend observed does not show any distinct optimum reached for both the catalytic and specific activity. However for mass activity, it increased and peaked at a Pd particle size of 5 nm before decreasing with any further increase of Pd particle size.^[67] Hence, by controlling/tuning the particle size, an optimal catalytic, specific and mass activity of Pd NPs can be achieved.

2.10.3 Manipulating Shape of Palladium Nanoparticles

It has also been reported by various researchers on manipulating the shape of Pd NPs to achieve increase catalytic and specific activity. One group has reported increased catalytic activity using cubic-shaped Pd NPs in comparison to spherical Pd NPs.^[68] Another group has also reported success in using Pd nanorods to increase both

catalytic and specific activity.^[69] In both cases, it was proven that by changing the shape of the Pd NPs, it improved the O₂ adsorption onto the desired (active) facets of the catalyst which in turn increased its activity. Hence, the manipulation of the shape of Pd NPs is also a viable research front in achieving increasing electrocatalytic activity.

2.10.4 Formation of Bimetallic Palladium Nanoparticles

Although Pd is cheaper with respect to Pt, Pd itself is still relatively expensive. Hence, there has been focus on using a combination of Pd and other alloys to increase the catalytic activity in ORR and FAO while reducing the overall amount of Pd needed.^[31, 44] Researchers have reported some success in using titanium (Ti) with Pd to increase catalytic activity^[63] while others have also reported limited success in using iron (Fe) as the other metal instead.^[64] Hence, although the catalytic activity (onset potential) in both ORR and FAO is better with respect to the industrial standards, these alloys are not cost efficient as the amount of the alloy needed is still relatively high. Even though using bimetallic Pd NPs have shown some advancements, there is still room for greater improvement in using such techniques in enhancing catalytic activity of Pd in ORR and FAO.

2.10.5 Using various support materials with Pd NPs

It was mentioned previously one of the interesting advancements in improving catalytic activity for Pd in ORR and FAO was using alloys. The concept in using support materials is also similar to that, which is to use cheap support materials (graphene, carbon etc) to lessen the amount of Pd needed.^[35, 70] In fact, the industrial

standard which is commonly applied in industries as well as in the evaluation of electrocatalyst in research is either platinum or palladium loaded carbon (Pt/C).^[13] There have been many successful reported cases of using graphene in particular to enhance the catalytic activity of Pd in ORR and FAO.^[35, 71-72] These reported cases have also shown that the enhancement was seen in catalytic, specific as well as mass activity of the Pd. Therefore using various support materials to enhance catalytic activity of Pd in ORR and FAO is a viable option with many interesting development opportunities with the abundance of such support materials.

2.10.6 Manipulating Morphology of Pd NPs

One of the most interesting advancements in enhancing catalytic activity of Pd NPs in ORR and FAO is manipulating the morphology of Pd NPs. This area of research has been sorely overlooked even though success has been reported using other metals such as nickel (Ni), cobalt (Co) and gold (Au).^[65, 73-74] These reported successes have not only been reported in electrocatalysts involving nanoparticles but even in films.^[66]

Typically in the manipulation of morphology, the amorphous variant of the metal is used to enhance the catalytic activity of the metal. These amorphous variants are achieved by introducing other elements such as nitrogen (N) or phosphorus (P) into the lattice structure.^[75] This introduction of other elements into the lattice to disrupt the crystal lattice and hence results in the metal changing from crystalline to amorphous. The theory behind using the amorphous variant is that the amorphous nature of the metal provides defects, kinks and edges in the structure which is not observed in the crystalline state.^[76-77] These defects, also known as low co-ordination sites, are shown to be preferential binding sites in which improvement to the catalytic activities of the

metals are observed.^[74, 78-80] Hence, using by manipulating the morphology and making amorphous catalysts is an interesting approach in enhancing the catalytic activity of Pd NPs in both ORR and FAO.

However, a problem with using such amorphous catalysts in general is due to the stability of these catalysts. These amorphous catalysts tend to be relatively unstable and will over time revert back to its crystalline state due to Gibb's free energy (lower energy state). Therefore, in this thesis, focus will be made to not only use amorphous Pd NPs to achieve enhancement in catalytic, specific and mass activity, but also to increase the longevity of these amorphous catalysts such that industrial applications for these catalysts are viable.

2.11 Bilirubin Oxidase

As reported earlier, for the ORR portion of BFC, BOD is the most commonly used enzyme. This is because compared to other enzymes such as laccase, BOD has the highest catalytic activity at near neutral pH range (pH 6-7) and has greater tolerance to chloride ions which can deactivate the enzymes.^[1]

Figure 7 shows the crystal structure of BOD (Myrothecium Verrucaria). BOD is a blue multicopper oxidase which catalyzes the oxygen into water through a four electron pathway. The substrate binding portion of BOD is known as T1 and contains one copper ion (Cu^{2+}) at the binding center. For the active site where the ORR takes place, it is known as T2 and T3, and contains a cluster of three copper centers. How BOD works is that electrons which come from the cathode (or redox mediator) are accepted at the T1 site and transferred to the T2/T3 copper cluster where ORR occurs.^[1, 21, 81]

Herein lies the problem with BOD or using enzymes in general. As mentioned earlier, one of the main shortcomings of using BOD is that the electron transfer between the electrode and the T1 site is poor due to poor binding orientation of the enzyme onto the substrate. Some researchers have used mediators such as 2,2'-Azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) to solve this problem but the presences of such mediators causes other problems such as voltage loss due to potential difference arising between the enzyme and mediator as well as the hazardous nature of the mediators which limits implantation applications.^[1, 21, 82]

Therefore, a better strategy would be to use substrates which can induce optimal binding of the BOD to it in order to increase electron transfer. Researchers have shown some progress with using gold and graphite to achieve such optimal bindings.^[1, 20-21, 83-84] Hence, this thesis will attempt to use Pd NPs to achieve such optimal binding and increase electron transfer rate and catalytic activity of BOD ORR.

Figure 7. Crystal structure of BOD (Myrothecium Verrucaria).^[1]

3. Experimental Procedure

3.1 Stock Solution Preparation

A 1 M of potassium hydroxide stock solution (KOH) (Sigma Aldrich) was prepared by dissolving 56.11 g of KOH pellets in 1 L of deionized (DI) water. This stock solution was stored at room temperature in a 1 L glass bottle. The 0.1 M of KOH solution used in the electrochemical experiment was prepared by diluting the 1 M of KOH solution by 10 times.

A 2M of formic acid stock solution (HCOOH) was prepared by diluting 94.863 mL of concentrated HCOOH (95% wt, Sigma Aldrich) to 1 L of DI water. This stock solution was stored at room temperature in a 1 L glass bottle. The 1 M of HCOOH solution used for the electrochemical experiment was prepared by diluting 2 M of HCOOH solution by 2 times.

The 2M of sulphur acid (H₂SO₄) was prepared by diluting 204.333 mL of concentrated H₂SO₄ (95-97%, Sigma Aldrich) to 1 L of DI water. This stock solution was stored at room temperature in a 1 L glass bottle. The 0.5 M of H₂SO₄ solution used in the experiment was prepared by diluting the 2M of H₂SO₄ by 4 times.

The 0.1 M of phosphate buffer solution (PBS) of pH 6.5 was prepared by dissolving 9.157 g of sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O) and 9.016 g of sodium phosphate dibasic heptahydrate (Na₂HPO₄·7H₂O) in 1 L of DI water. The stock solution was stored at room temperature in a 1 L glass bottle.

The 0.2 M of sodium hypophosphite monohydrate (NaH₂PO₂) (98% wt, Alfa Aesar) solution was prepared by dissolving 2.119 g of NaH₂PO₂ in 100 mL of DI water. This solution was stored at room temperature in a 100 mL glass bottle.

The 0.2 M of hydrazine hydrate solution (N_2H_4) (50-60% wt, Sigma Aldrich) was prepared by diluting 1.165 mL of N_2H_4 into 100 mL of Di water. This solution was stored at room temperature in a 100 mL glass bottle.

The 20 mM solution of palladium (II) chloride (PdCl_2) (99% wt, Sigma Aldrich) was prepared by dissolving 0.3546 g of PdCl_2 into 99 mL of water with 1 mL of concentrated hydrochloric acid (HCl). This stock solution was stored at room temperature in a 100 mL glass bottle. The 2mM of PdCl_2 used in the electrochemical experimentation was prepared by diluting the 20 mM stock solution by 10 times.

The 5 g L^{-1} solution of carbon nanotubes (CNT) (O.D. x Length 6-13 nm x 2.5-20 μm , Sigma Aldrich) was prepared by dissolving 50 mg of CNT in 10 mL of N,N-Dimethylformamide (DMF) (99.8%, Sigma Aldrich) as described elsewhere.^[85-86] This stock solution was stored at room temperature in a 20 mL glass bottle.

The 8 mg mL^{-1} solution of BOD solution (2.06 U/mg, Sigma Aldrich) was prepared by dissolving 8 mg of BOD in 1 mL of 0.1 M pH 6.5 PBS. This solution was stored at 5 °C in a 20 mL glass bottle.

The 10 mg mL^{-1} of 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) (10 mg, Sigma Aldrich) was prepared by dissolving the 10 mg tablet of ABTS in 1 mL of 0.1 M pH 6.5 PBS. This solution was stored at 5 °C in a 20 mL amber glass bottle further wrapped in aluminium foil to ensure it is not exposed to light.

Table 3. Summary of concentration of chemicals used for different experiments.

Experiment	Chemical Used
Electroless Deposition	0.2 M NaH_2PO_4 0.2 M N_2H_4 2 mM PdCl_2
Oxygen Reduction Reaction	0.1 M KOH
Formic Acid Oxidation	1 M HCOOH 0.5 M H_2SO_4
Bio-fuel Cell	0.1 M pH 6.5 PBS 5 g L^{-1} CNT 8 mg mL^{-1} BOD 10 mg mL^{-1} ABTS

3.2 Stepwise Electroless Deposition of Palladium Nanoparticles

The Pd NPs were synthesized directly onto rotating disc glass carbon electrode (RDE-GC) (3 mm in diameter, Bioanalytical Systems, Inc.) by stepwise electroless deposition. Firstly, for the synthesis of amorphous Pd NPs, the RDE-GC was polished with alumina polish (0.05 μm) and washed thoroughly with DI water. It was also water bath sonicated in both ethanol and water for 5 minutes each respectively and rinsed thoroughly with DI water again before use. Next, the RDE-GC was dipped into a solution containing the reducing agent solution (0.2 M NaH_2PO_2 solution) for 10 s. It was then quickly air blown dry and dipped into another solution containing 0.2 M PdCl_2 for another 10 s. Subsequently, the RDE-GC was washed with DI water before being air blown dry again. This constitutes 1 deposition cycle. For the synthesis of

crystalline Pd NPs, the same process was repeated with the only change being the change of reducing agent from NaH_2PO_2 to N_2H_4 .

3.3 Preparation of Platinum and Palladium loaded Carbon

The Pt/C electrocatalyst was prepared according to the procedure described elsewhere.^[87] First, 100 mg of Pt/C powder (20% Pt on Vulcan XC72, Sigma-Aldrich) was dispersed in 100 mL of ethanol, and the mixture was ultrasonicated before use. 7.5 μL of Pt/C was cast onto the RDE-GC (polished with the method described above) using a microsyringe. This same procedure was repeated for the preparation of Pd/C electrocatalyst as well.

3.4 Preparation of Bilirubin Oxidase Biocathode

Firstly, the CNT in DMF was ultrasonicated for 30 minutes before use. Next, 20 μL of CNT was drop casted onto the RDE-GC (polished with method described above) using a microsyringe and allowed to dry overnight. Next, Pd NPs were coated onto the CNT using the stepwise electroless deposition method described above. Following this, 20 μL of BOD was casted onto the RDE-GC surface and allowed to dry for 2 hours in a dessicator before use.

3.5 Linear Sweep Voltammetry for Oxygen Reduction Reaction

Linear sweep voltammetry (LSV) were performed to analyse the ORR properties of the electrocatalysts. The LSV was conducted in a typical 3 cell setup. The working electrode used was the RDE-GC loaded with the desired electrocatalyst to be analyzed

while a platinum wire was used as the counter electrode. The reference electrode used was Ag/AgCl (KCl saturated). All the potentials for ORR were referenced to reversible hydrogen electrode (RHE). The conversion is shown in Equation 11:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.199 \text{ V} \quad (11)$$

All the LSV was conducted in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mVs⁻¹ and a rotational speed of 400, 900, 1600, 2500 rpm unless otherwise stated. The LSV was recorded in a direction of 0.166 V to 0.966 V vs RHE.

All the electrochemical measurements were conducted on a Princeton Applied Research VersaSTAT3-200 potentiostat.

3.6 Cyclic Voltammetry for Formic Acid Oxidation

The setup for the cyclic voltammetry (CV) measurement was similar to that of LSV. The CV was conducted in a N₂-saturated 0.5 M H₂SO₄ and 1 M HCOOH mixture at a scan rate of 50 mVs⁻¹ with no rotation. For FAO, the potentials are kept with reference to the original Ag/AgCl (KCl saturated) for easier comparison to other reference papers. The CV was recorded in a range of -0.2 V to 1 V vs Ag/AgCl (KCl saturated).

3.7 Cyclic Voltammetry for Electrochemically Active Surface Area Measurement

The setup for the CV measurement was similar to that of LSV. The CV was conducted in N₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ solution at a scan rate of 50 mVs⁻¹ with no rotation. The CV was recorded in a range of 0.041 V to 1.266 V vs RHE for ORR and in a range of -0.3 V to 1.2 V vs Ag/AgCl (KCl saturated) for FAO. The CV for each sample was repeated for 10 cycles.

3.8 Preparation of Inductively Coupled Plasma-Mass Spectrometry

For the extraction of the Pd nanoparticles for inductively coupled plasma-mass spectrometry (ICP-MS) analysis, 5 μ L of concentrated HNO₃ solution (Sigma Aldrich) was dripped carefully using a microsyringe on the RDE-GC for 5 min. Following which, 2 μ L of HNO₃ was extracted twice with care and dispersed into two separate plastic tubes containing 500 μ L each of DI water. Both samples were then analyzed with an ICP-MS (Agilent 7700) equipped with a 3rd generation He collision/reaction cell to minimize interferences. LSV measurements were performed before and after the extraction to ensure that the Pd nanoparticles were fully extracted (i.e., the CV obtained after the extraction was same as the blank LSV or CV).

3.9 Transmission Electron Microscopy / Scanning Transmission Electron Microscopy preparation

The transmission electron microscopy (TEM) samples were prepared by using the stepwise electroless deposition on standard copper (Cu) specimen grid (Formvar/Carbon on 300 mesh, JEOL Asia Pte Ltd). The TEM grid was prepared by

first holding it in place with adhesive tape onto a clean disposable glass slide for easy handling. Firstly, the reducing agent solution was dripped onto the TEM grid using a disposable pipette such that the entire grid was covered with the reducing agent for 10 s. The grid was subsequently air blown dry. Next, the PdCl_2 solution was dripped onto the TEM grid as well for 10 s. DI water was then used to wash the TEM grid thoroughly before being air blown dry again. The TEM sample was allowed to dry overnight in a dessicator. The TEM sample was then observed using JEM-2010 microscope (JEOL Ltd.) operated at 200 kV. The TEM sample was used for STEM observation as well. The TEM used was a FEI-Titan 80/300 scanning/transmission electron microscope operated at 200 kV.

3.10 Scanning Electron Microscopy preparation

The scanning electron microscopy (SEM) was prepared using the stepwise electroless deposition on a glassy carbon plate (1 mm thick, Alfa Aesar). The glassy carbon plate was first held in place with an adhesive tape onto a clean disposable glass slide for easy handling. Firstly, the reducing agent solution was dripped onto the glassy carbon plate using a disposable pipette such that the entire plate was covered with the reducing agent for 10 s. The plate was subsequently air blown dry. Next, the PdCl_2 solution was dripped onto the glassy carbon plate as well for 10 s. DI water was then used to wash the glassy carbon plate thoroughly before being air blown dry again. The SEM sample was allowed to dry overnight in a dessicator. The SEM was observed using a JSM-7600F (JEOL Ltd.) microscope operated at 5.0 kV.

3.11 Preparation of X-ray Diffraction Samples

The X-ray diffraction (XRD) samples were prepared by mixing the reducing agent and the PdCl₂ solution to give Pd powder. This was due to the fact that the loading of the Pd nanoparticles onto both glass, glassy carbon as well as silicon wafer substrates were too little to be detected by the XRD. Hence, 0.2 M of the reducing agent was mixed with 2 mM of the PdCl₂ solution (similar conditions to the electroless deposition method) to give finely dispersed Pd powder. This powder was washed thoroughly with DI water and dried over night in a dessicator before being tested. The XRD was conducted using PANalytical Empyrean diffractometer equipped with a Cu K α radiation source ($\lambda = 1.54060 \text{ \AA}$).

3.12 Preparation for Ultra Violet-Visible Light Spectroscopy

The ultra violet-visible light (UV-Vis) was prepared by using filling a quartz cuvette (Shimadzu) with 2 mL of 0.1 M pH 6.5 PBS. For calibration, a known amount of 7 mg mL⁻¹ BOD (0.005, 0.01, 0.02 and 0.03 μ L) was added to the cuvette. Following that, 100 μ L of ABTS was added to the cuvette and a UV-Vis was conducted after 120 seconds with reference to literature.^[8, 88] For the UV-Vis scan, the scan was ran from 450 nm to 400 nm. The peak at 420 nm was taken and used to plot the calibration curve. For the measurement the samples, the preparation is almost similar. The biocathode synthesized from the above mentioned procedures was washed thoroughly and soaked in the cuvette containing 2 mL of 0.1 M pH 6.5 PBS and 100 μ L of ABTS. After 120 seconds, the biocathode was removed and the UV-Vis scan was conducted. The UV-Vis was conducted using Shimadzu UV-2600.

4. Results and Discussions for Oxygen Reduction Reaction

4.1 Synthesizing the Palladium Nanoparticles

As mentioned previously, there is a need for an alternative method for synthesizing Pd NPs which is both facile and simple. Therefore, this thesis has developed a new stepwise electroless deposition method to synthesize the Pd NPs onto the RDE-GC directly.

The inspiration for such a method came from electroless deposition process which is a popular process in Ni plating but has not seen much use otherwise.^[89] There are several reasons for the choice of using electroless deposition for Pd NPs synthesis.

Firstly, the stepwise electroless deposition process is able to synthesize the Pd NPs directly onto the electrode surface. This eliminates the need to synthesize the Pd NPs separately and casting it onto the electrode surface. Such separate preparation and storing of the Pd NPs beforehand gives rise to several issues such as the need to extend the shelf life of Pd NPs by using additives (prevent Pd NPs aggregation). These additives might adversely affect the overall electrocatalytic properties of the Pd NPs as it can block electron transfer as well as mass transport.^[90-91] Also, further additives are also required when casting the Pd NPs onto the electrode to ensure better dispersion of the Pd NPs on the surface which might affect the catalytic activity even more.^[26]

Next, this electroless deposition method is also remarkably facile and simple (sequential dipping into different reagents). The required reaction time for each deposition cycle is short (approximately 20 s). This is significantly better than traditional methods where complicated procedures and conditions (high temperature or vacuum) are needed.^[35, 62-63]

Moreover, by using this stepwise electroless deposition method, less chemical waste is produced. This is due to the fact that the amount of metal consumed in the reaction is actually the metal which has been deposited onto the electrode surface. This is in contrast to traditional synthesis method (both electrical and chemical) where the amount of waste generated is quite high.

Lastly, this electroless deposition method is a superior method in loading Pd NPs onto the desired substrates. In typically industrial application of electrocatalysts in fuel cell, the Pd NPs are usually mixed with a carbon paste to be spread and deposited onto the substrate. However, a severe limitation is that the substrate can be only of simple design or structure. Unlike such a case, electroless deposition allows deposition of the Pd NPs onto complex structure which bypass this traditional limitations which opens up the possibility for more unique substrates used.

4.2 Characterizing the Palladium Nanoparticles

Before the further experimentation is conducted on the Pd NPs synthesized by the proposed electroless deposition method, there is a need to characterize them. Hence, TEM was conducted on both the Pd samples prepared using NaH_2PO_2 and N_2H_4 as reducing agents.

Figure 8A shows the TEM image of the Pd NPs sample prepared by NaH_2PO_2 reducing agent (Pd-P). As seen from the TEM image, the Pd-P NPs are small (approximately 3-5 nm in diameter) and sparsely dispersed. From the halo-shaped electron diffraction, it clearly proves that the Pd-P NPs are amorphous in nature. This prove is further supported by broadening of the Pd peaks in the XRD profile shown in Figure 9. Also from the EDS spectra Figure 4A, the Pd-P NPs contains 11 at% of P and 89 at% of Pd.

On the other hand, in Figure 8B, the Pd NPs sample prepared using N_2H_4 as reducing agent (Pd- N_2H_4) shows that the Pd- N_2H_4 NPs are relatively similarly sized to the Pd-P NPs and also quite well dispersed. However from the electron diffraction, Debye-Scherrer rings indicate clearly that the Pd- N_2H_4 NPs are crystalline. This is also further supported as seen from the sharp Pd XRD profile seen in Figure 9. In addition, the EDS spectra in Figure 8B shows that the Pd- N_2H_4 NPs contains only Pd.

Figure 8. Transmission electron microscopy (TEM) images, electron diffraction patterns and energy-dispersive X-ray spectroscopy results from Pd NPs by the stepwise electroless deposition process using reducing agents (A) NaH_2PO_2 and (B) N_2H_4 . From the EDS spectra, Pd:P ratio for (A) is 89:11, whereas that for (B) indicates that the particles are pure Pd.

Figure 9. X-ray diffraction (XRD) patterns of Pd deposits obtained by mixing 2 mM PdCl_2 solution (1 mL) with (A) 0.2 M NaH_2PO_2 or (B) 0.2 M N_2H_4 solution (1 mL).

4.3 Oxygen Reduction Reaction Polarization Curves of Palladium Nanoparticles

The ORR polarization curve of the Pd NPs were analyzed to determine the electrocatalytic effect of the Pd NPs on ORR. The results of the ORR polarization curves of both amorphous Pd-P and crystalline Pd-N₂H₄ NPs are compared with commercially obtained Pt/C and Pd/C (similar to literature) as shown in Figure 10.^{[92-}

^{96]} It clearly illustrates that with just 3 deposition cycles using the electroless deposition method with either reducing agent, the Pd NPs exhibit superior catalytic activity compared to Pt/C and Pd/C as indicated from the positive shift in the ORR polarization curve. This positive shift in the ORR polarization is indication that the onset potential of the ORR is increased and therefore is occurring at earlier rate. This demonstrates the different effect that different catalysts has on ORR. In addition, this positive shift in the ORR polarization curve is seen to increase with increasing number of deposition cycles. This trend was observed in both the Pd-P and Pd-N₂H₄ NPs at all deposition cycles. However, this comparison is just qualitative and hence more accurate examination is required.

The half-wave potential of the Pd NPs synthesized using the electroless deposition method was compared to commercially obtained Pt/C and Pd/C to give a more accurate analysis of the increment in catalytic activity. The more positive the half-wave potential of the ORR polarization curve, the better the catalytic activity of the electrocatalysts. As summarised in Table 4, Pt/C has the lowest half-wave potential at 0.74 V. All the Pd electrocatalysts exhibited higher catalytic activity compared to Pt/C. Next, comparison was made between the commercial Pd/C in contrast to the Pd NPs synthesized by the proposed electroless deposition method. At almost all the deposition cycles, Pd NPs synthesized by the proposed method gave similar or more

positive half-wave potential value than Pd/C (0.83 V). The only exception was the 3 deposition cycles Pd-N₂H₄ NPs (0.78 V) which was lower than Pd/C. Overall, the Pd NPs synthesized by the proposed electroless deposition method exhibited higher catalytic activity in comparison to Pt/C and Pd/C.

Next, the difference in catalytic activity between the Pd-P and Pd-N₂H₄ NPs was analyzed. At similar number of deposition cycles, Pd-P always exhibited higher catalytic activity than Pd-N₂H₄ as seen from its higher half-wave potential. At 3 deposition cycles, Pd-P exhibited a more positive half-wave potential (0.82 V) than Pd-N₂H₄ (0.78 V). In fact, at just 3 deposition cycles, Pd-P showed a half-wave potential similar to that of 9 and 18 cycles of Pd-N₂H₄ (0.83 V and 0.82 V respectively). Therefore as expected, 9 and 18 cycles of Pd-P exhibited even higher half-wave potentials than their corresponding Pd-N₂H₄ counterparts (0.85 V and 0.88 V respectively). On the whole, the half-wave potential of Pd-P NPs seems to increase with increasing deposition while Pd-N₂H₄ NPs seems to reach a maximum at 9 deposition cycles even though the onset potential increases.

Figure 10. ORR polarization curves for Pd nanoparticles synthesized with (A) NaH_2PO_2 and (B) N_2H_4 . The numbers correspond to the cycle numbers of the stepwise electroless deposition process. The measurements were performed in 0.1 M O_2 -saturated KOH solution. Scan rate: 10 mVs^{-1} . Rotational speed: 1600 rpm

Table 4. Half-wave potential values of Pd and Pt obtained from Figure 9.

Catalyst	Half-Wave Potential (V)
Pt/C	0.74
Pd/C	0.83
Pd-P (3)	0.82
Pd-N_2H_4 (3)	0.78
Pd-P (9)	0.85
Pd-N_2H_4 (9)	0.83
Pd-P (18)	0.88
Pd-N_2H_4 (18)	0.82

4.4 Calculation and Analysis of the Specific Activity of Palladium Nanoparticles in Oxygen Reduction Reaction

Although the half-wave potential demonstrates that Pd NPs synthesized by the proposed electroless deposition has better catalytic activity than commercial Pt/C and Pd/C, a more accurate assessment is needed. One way of accurately assessing the differences in electrocatalysts is by their specific activity (i_s) (kinetic current (i_k) normalized by electrochemically active surface area (ECSA)). Hence, the i_s of the Pd NPs, Pt/C and Pd/C are calculated, analyzed and compared.

In order to calculate the i_s , the i_k must first be obtained. Therefore, to obtain the i_k , the Koutecky-Levich (K-L) equation (Equation 8) needs to be used and hence, the i_d needs to be known. To obtain the i_d , the electrocatalysts needs to be rotating when the ORR polarization is conducted. The i_d can then be easily obtained from the ORR polarization graph as it is the point where the current density reaches maximum and stabilizes.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (8)$$

However, there is a need to verify whether the i_d obtained from the graph is correct. In order to do so, the K-L plot of the electrocatalysts needs to be plotted. Not only does the K-L plot allows us to check if the value for i_d is correct, it will allow us to calculate the number of electrons involved in the ORR. Therefore to obtain the K-L plot of the different electrocatalysts, the ORR polarization curve of these electrocatalysts at different rotating speeds are conducted. Shown in Figure 11 is the representative ORR polarization curve of each of the electrocatalysts at different rotation speed.

From the ORR polarization curves at different rotating speed, the K-L plots can be obtained. Figure 12 shows the representative plots of the K-L plot of each of the corresponding electrocatalysts. The K-L plot was plotted at 2 different potentials, one at 0.60 V and the other at 0.50 V. These 2 potentials were selected as they are near the potential at which the diffusion limit current (i_d) is present. The i_d can be easily obtained from the ORR polarization graph as it is the point where the current density reaches maximum and stabilizes.

First, analysis on the K-L plot for the 0.50 V is made. As seen in Figure 12, most of the K-L plots at 0.50 V passes very close to the origin. Furthermore, additional information which can be obtained from the K-L plot at 0.50 V would be the number of electron transfer that the electrocatalysts promotes. This value can be acquired by using the previously mentioned Equation 10. From Equation 10, since all the values except n are known, the number of electron transfer can be easily calculated. The reason why the K-L plot at 0.50 V is used instead of the K-L plot at 0.85 V is because the current density fluctuates too much at 0.85 V which makes the number of electron calculated at that potential inaccurate.

$$B = 0.62nFS C_0 D^{\frac{2}{3}} \nu^{-\frac{1}{6}} \quad (10)$$

Moving on, the K-L plot at 0.60 V is analyzed. From the K-L plot, it is seen that the gradient of the plot at 0.60 V is relatively similar to that of 0.50 V. This demonstrates that the electron transfer at both potentials are similar.

Finally, with the number of electrons and i_d value known, the i_k value at 0.85 V can be calculated again from Equation 8 with the i value obtained directly from the ORR polarization curve at 1600 rpm.

Figure 11. ORR polarization curves for Pd-P, (A) 3 cycles, (B) 9 cycles (C) 18 cycles, Pd-N₂H₄, (D) 3 cycles, (E) 9 cycles, (F) 18 cycles, (G) Pt/C and (H) Pd/C conducted at 400, 900, 1600 and 2500 rpm. Scan rate: 10 mVs⁻¹. These are the represented graphs for each of the corresponding electrocatalysts.

Figure 12. K-L plot for Pd-P, (A) 3 cycles, (B) 9 cycles (C) 18 cycles, Pd-N₂H₄, (D) 3 cycles, (E) 9 cycles, (F) 18 cycles, (G) Pt/C and (H) Pd/C. This is a represented graph for each of the corresponding electrocatalysts.

With the i_k value known, the next step in the obtaining the i_s is acquiring ECAS which requires the full CV curve of the electrocatalysts in N_2 -saturated solution. By acquiring the full CV, the reduction charge value of the electrocatalysts can be calculated. By using the reduction charge value in literature, the ECAS can be obtained correspondingly. It is important to note that the full CV needs to be conducted in N_2 -saturated solution to avoid the reduction charge associated with ORR.

The calculation of the reduction charge of the full CVs of the Pd and Pt is different. The full CV of Pd is first analyzed. Figure 15 show the representative view of the full CV of each corresponding electrocatalysts of Pd conducted in N_2 -saturated solution. For explanation purposes, 9 cycles Pd-P in Figure 13 is used. For Pd, the reduction charge arises from the reduction of PdO to Pd. As seen in Figure 13, the reduction charge is calculated from 0.5 V to 0.9 V. This is the known region for the reduction of PdO to Pd. However, the actual desired reduction charge area is labelled as Region 1

Figure 13. Full CV of 9 cycles Pd-P swept from 0.04 V to 1.27 V in N_2 -saturated 0.1 M KOH solution. This is a represented graph for all the Pd electrocatalysts.

as seen in Figure 13. Region 2 is known as the double layer capacitance discharge which needs to be eliminated in the calculations. Hence, with the reduction charge of PdO known to be $405 \mu\text{C cm}^{-2}$, the ECSA of the Pd electrocatalysts can be calculated.

For Pt, the calculation of the Pt charge is different from Pd. Figure 14 shows the representative view of the full CV of Pt/C conducted in N_2 -saturated solution. For Pt, the Pt charge calculated is a result from hydrogen adsorption and desorption on Pt. From Figure 14, the charge associated with hydrogen desorption on Pt is marked by the Region 1 and 2. Hence, the charge is calculated from the potential range of 0.04 V to 0.45 V. However, the actual desired charge area is Region 1 with Region 2 being the double layer capacitance discharge. Therefore, Region 2 needs to be subtracted from the calculations. With the reduction charge of hydrogen adsorption and desorption known to be $210 \mu\text{C cm}^{-2}$, the ECSA for the Pt/C electrocatalysts can be calculated accordingly.

Figure 14. Full CV of Pt/C swept from 0.04 V to 1.27 V in N_2 -saturated 0.1 M KOH solution. Scan rate: 50 mVs^{-1} . This is a represented graph for all the Pt electrocatalysts.

Figure 15. Full CV of Pd-P, (A) 3 cycles, (B) 9 cycles (C) 18 cycles, Pd-N₂H₄, (D) 3 cycles, (E) 9 cycles, (F) 18 cycles, (G) Pt/C and (H) Pd/C conducted in N₂-saturated solution and swept from 0.04 V to 1.27 V vs RHE. Scan rate: 50 mVs⁻¹. This is a represented graph for each of the corresponding electrocatalysts.

Table 5 summarizes the results of the calculations for the number of electrons transferred and the i_s . Firstly, the results for the number of electrons transferred is evaluated. Overall, almost all of the Pd NPs synthesized by the proposed electroless deposition method gave electron transfer of 4. This is in contrast to the Pt/C (3.03 electrons) and Pd/C (2.35 electrons) which gave significantly less electron transferred. This result implies that the Pd NPs synthesized by the proposed method is more efficient as it gave the highest number of electron transferred as compared to the commercial Pt/C and Pd/C. Next, comparison is made between the Pd-P and the Pd-N₂H₄ NPs. The Pd-P produced a consistent 4 electron transfer for all the deposition cycles while Pd-N₂H₄ gave 4 electron transfer at only 9 and 18 deposition cycles. 3 cycles Pd-N₂H₄ gave suboptimal electron transfer of 2.42 which was the second lowest electron transfer out of all the electrocatalysts.

Moving on, the i_s of all the electrocatalysts are compared next. Pt/C had the lowest i_s (0.47 mA cm⁻²) followed by the Pd/C (1.58 mA cm⁻²). This is in contrast to the Pd NPs synthesized by the proposed electroless deposition method which had significantly higher i_s . What this implies is that the amount of current produced per unit of active surface area of Pt/C and Pd/C electrocatalysts is very low with respect to the Pd NPs. It is also interesting to note that the i_s of the Pd NPs increases with increasing deposition cycles. The i_s of Pd-P and the Pd-N₂H₄ NPs are compared with each other next. At every deposition cycle, Pd-P gave higher i_s as compared to Pd-N₂H₄. This difference becomes significantly more pronounced at higher deposition cycles. The i_s of 3 cycles Pd-P was 1.1 times higher than 3 cycles Pd-N₂H₄ while 9 cycles Pd-P was 1.8 times better than 9 cycles Pd-N₂H₄ and finally 18 cycles of Pd-P was 1.9 times greater than 18 cycles of Pd-N₂H₄. Hence, Pd-P is superior to Pd-N₂H₄ in terms of i_s . It is also noticed that the i_s for the Pd-P was much higher at higher deposition cycles (9

and 18 cycles) than low cycles. This would suggest that the initial Pd-P NPs synthesized on the glassy carbon surface of the GC-RDE was not as active as the subsequently synthesized Pd-P, which are deposited on the previously deposited Pd-P NPs.

Table 5. Number of electrons transferred and specific activity values of Pd and Pt

Catalyst	Number of Electrons Transferred (n)	Specific Activity (i_s) (mA cm ⁻²)
Pt/C	3.03	0.47 ± 0.01
Pd/C	2.35	1.58 ± 0.02
Pd-P (3)	4.17	2.31 ± 0.59
Pd-N₂H₄ (3)	2.42	2.16 ± 0.29
Pd-P (9)	4.22	5.16 ± 0.68
Pd-N₂H₄ (9)	3.65	2.87 ± 0.33
Pd-P (18)	4.24	6.85 ± 0.64
Pd-N₂H₄ (18)	3.96	3.53 ± 0.58

4.5 Calculation and Analysis of the Mass Activity of Palladium Nanoparticles in Oxygen Reduction Reaction

As mentioned previously, since one of the main attractions for using Pd as a replacement for Pt is the reduced cost, it is important to know the amount of Pd that is loaded onto the GC-RDE. A more accurate representation would be to calculate the i_m (i_k normalized by Pd load). Therefore, by comparing the i_m of the electrocatalysts, the cost efficiency of the electrocatalysts can be evaluated which has industrial significance.

In order to calculate the i_m , firstly, the amount of Pd which is loaded onto the GC-RDE needs to be made known. In the proposed electroless deposition process, the amount of Pd loaded cannot be simply calculated as the amount loaded varies from each cycles. Therefore to accurately calculate the amount of Pd NPs loaded onto the GC-RDE, the Pd NPs needs to be extracted from the electrode surface and quantitatively analyzed through ICP-MS. Hence, after completing all the necessary scans (ORR polarization and full CV curves), the amount of Pd loaded was extracting from the electrode surface. This was done by using concentration HNO_3 to dissolve away the Pd NPs on the electrode surface. After which, the concentrated HNO_3 was collected and diluted before sending for ICP-MS. To ensure that all the Pd NPs were extracted from the surface of the electrode, the ORR polarization curve was ran again to ensure that it gave a curve similar to that of a uncoated GC-RDE as shown in Figure 16. Figure 16 shows the representative image of the ORR polarization before and after the extraction (9 Cycles Pd-P). It is seen from Figure 16 that after the extraction process, the ORR polarization curve actually becomes less active than even blank. This is indicative of 2 things. Firstly, this means that all of the Pd NPs has been successfully extracted from the surface. Hence there is no more catalytic activity observed in the ORR polarization

curve. Secondly, this also suggest that HNO_3 deactivates the GC-RDE surface which results in the ORR polarization curve being less active than blank. A thing to note is that this extraction method and ICP-MS measurement was not required for Pt/C and Pd/C as the amount loaded can be simply calculated as the preparation for these electrocatalysts is made through casting.

Figure 16. ORR polarization curve of blank GC-RDE and 9 cycles Pd-P in O_2 -saturated 0.1 M KOH solution before and after HNO_3 extraction. Rotation speed: 1600 rpm. Scan rate: 10 mV s^{-1} . This is a represented graph for all the Pd electrocatalysts.

Table 6 summarises the mass activity of all the electrocatalysts. The results calculated are the averages of several number of repeated experiments. As tabulated in Table 4, Pt/C ($0.068 \text{ mA } \mu\text{g}^{-1}$) has the lowest mass activity followed by Pd/C ($0.17 \text{ mA } \mu\text{g}^{-1}$). Even the lowest mass activity achieved by the proposed electroless deposition method [3 cycles Pd- N_2H_4 ($1.11 \text{ mA } \mu\text{g}^{-1}$)] was 6.5 times greater than Pd/C, which was the highest mass activity for the commercial electrocatalysts. Hence, the Pd NPs synthesized by the proposed electroless deposition method is more cost efficient than the commercial electrocatalysts available.

Next comparison is made between the Pd-P and Pd-N₂H₄ NPs. At almost all the deposition cycles, Pd-P is seen to have higher mass activity compared to Pd-N₂H₄. From Table 6, the mass activity of 3 cycles Pd-P (1.79 mA μg^{-1}) was 1.6 times greater than 3 cycles Pd-N₂H₄ (1.11 mA μg^{-1}) while the mass activity of 9 cycles Pd-P (2.21 mA μg^{-1}) was 1.7 times greater than 9 cycles Pd-N₂H₄ (1.33 mA μg^{-1}). For 18 cycles, the mass activity for Pd-P was almost similar to that of N₂H₄. This conclusively proves that the Pd-P is more cost efficient than Pd-N₂H₄. On a similar note, the mass activity of the Pd-P sample produced from the proposed electroless deposition method has the highest value out of all the reported value. The 9 cycles Pd-P (2.21 mA μg^{-1}) which was the highest mass activity achieved in the proposed method was 2.6 times higher than the ones reported in literature.^[35] Hence, not only does the Pd NPs synthesized by the proposed electroless deposition method have higher mass activity (more cost efficient) than commercial electrocatalysts, amorphous 9 cycles (Pd-P) has the highest known mass activity value reported so far. It is speculated that the mass activity is highest at 9 cycles Pd-P because the stacking of the Pd NPs at 9 deposition cycles is the most optimal. This means that further deposition would only result in Pd NPs which are not in contact with the electrolyte and therefore wasted. In conclusion, the proposed electroless deposition method, especially in the case for the Pd-P, can be considered for industrial applications.

Table 6. Mass activity values of Pd and Pt electrocatalysts

Catalysts	Mass Activity (mA μg^{-1})
Pt/C	0.068 ± 0.001
Pd/C	0.17 ± 0.01
Pd-P (3)	1.79 ± 0.42
Pd-N₂H₄ (3)	1.11 ± 0.22
Pd-P (9)	2.21 ± 0.21
Pd-N₂H₄ (9)	1.33 ± 0.12
Pd-P (18)	1.34 ± 0.41
Pd-N₂H₄ (18)	1.44 ± 0.23

4.6 Importance of Amorphous Nature and Industrial Application of Palladium Nanoparticles in Oxygen Reduction Reaction

In the previously section, the superiority of the Pd NPs synthesized by the proposed electroless deposition method compared to commercial Pt/C and Pd/C has been demonstrated. However, there is a need to test the proposed deposition method on industrial substrates to check the viability of it industrialwise.

In typical fuel cell for industrial application, a catalyst sheet, traditionally carbon cloth is used. Usually, the electrocatalysts (eg. Pt) are made into carbon paste and spread onto carbon cloth to make the catalyst sheet.^[97-98] Hence, there is a need to see if the proposed electroless deposition method works not only with GC-RDE but with carbon cloth as well.

Figure 17 shows the ORR polarization curves of 9 cycles Pd-P and Pd-N₂H₄ deposited on carbon cloth by the proposed electroless deposition. This conclusively proves that the proposed method is applicable in industries. Furthermore, the catalytic activity of the Pd NPs can be actively tuned by changing the number of deposition cycles which give the proposed method even greater flexibility. Hence, the proposed electroless deposition method has many advantages over traditional catalysts synthesis in industrial application.

It is also noticed in the previous sections that amorphous Pd-P has higher catalytic, specific and mass activity compared to crystalline Pd-N₂H₄. Hence, it is important to experiment to see if the amorphous nature is the key factor in the superior catalytic properties of Pd-P over Pd-N₂H₄.

Again from Figure 17, it is shown that both the carbon cloth with 9 cycles of Pd-P as well as Pd-N₂H₄ were annealed at 700 °c for 1 hour. This temperature and duration has

been proven in literature to change the morphology of amorphous Pd to crystalline.^[99] Figure 17 shows that after annealing, both the catalytic activity for Pd-P and Pd-N₂H₄ decreases and becomes similar to each other. This would strongly suggest that the amorphous nature of Pd-P is key factor in its superior catalytic properties over Pd-N₂H₄. However, there is still the need to prove that the amorphous nature of Pd-P and not the P itself is the important feature. Figure 18 shows the EDS data of the Pd-P sample after the annealing. It clearly shows the presence of P remaining in the Pd-P sample after annealing. This conclusively proves that the amorphous nature is in fact the unique feature of the Pd-P NPs which gives its superior catalytic, specific and mass activity over crystalline Pd-N₂H₄ as well as the commercial Pt/C and Pd/C electrocatalysts.

It is theorized that the amorphous nature of the Pd NPs contributes to its superior catalytic, specific and mass activities due to the fact that the amorphous Pd NPs are more structurally disordered and contains more reactive and accessible sites. These sites, also known as low co-ordination sites, are represented by defects, edges and kinks, which are numerous in amorphous but not crystalline structures.^[79, 100] The presence of these low co-ordination sites have been previously shown to improve the catalytic activity for ORR.^[76, 78-79, 101]

Also, a recent study has shown that an increase in Pd-Pd bond length due to B doping led to lower binding energies for O₂ and O to Pd which optimizes both the dissociative adsorption of O₂ and reduction of O on Pd surface. These lower binding energies reduced the reaction barrier of the rate determining step of ORR and resulted in higher catalytic activity for the B doped Pd (Pd-B).^[102] This thesis strongly believe that the results reported in the previously mentioned work was observed here as well. From the XRD image in Figure 9, there was a downward shift in Bragg's angle (0.9 °) when

comparing the amorphous Pd-P (39.3 °) to the crystalline Pd-N₂H₄ (40.2 °). This downward shift would imply that due to P doping, the overall Pd-Pd bond length was likely to have increased in Pd-P which would explain the superior catalytic activity. However, due to the amorphous nature of Pd-P, it is difficult to use computational modelling to prove the above mentioned theory. Therefore, further experimentation such as high energy XRD and pair distribution function analysis (PDF) is required to obtain the Pd-P structure for modelling and has been proposed in future work.

Figure 17. ORR polarization curves of 9 cycles Pd nanoparticles synthesized on carbon cloth. Annealing was performed at 700 °C for 1 h. The measurements were performed in 0.1 M O₂-saturated KOH solution. Scan rate: 10 mV s⁻¹.

Figure 18. EDS of 9 cycles Pd P after annealing at 700 °c for 1 hour. The Pd:P ratio for is 90:10.

4.7 Durability Test for Palladium Nanoparticles in Oxygen Reduction Reaction

It has already been shown that Pd NPs synthesized by the proposed electroless deposition method are superior to that of commercial Pt/C and Pd/C in all the catalytic aspects including catalytic, specific and mass activities. However, one of the remaining experimentation left to conclude that Pd NPs synthesized by the proposed method is superior is the durability test.

It was mentioned earlier that the long term durability of Pt in general is a huge liability in using Pt in fuel cell. Therefore, there is need test if the long term durability of the Pd NPs of the proposed method are superior to that of the commercial catalysts. Hence, the chronoamperometric response of the electrocatalysts are conducted and evaluated.

Figure 19 shows the chronoamperometric response of the electrocatalysts. Firstly, comparison is made between the commercial Pt/C and Pd/C against the Pd NPs synthesized by the proposed electroless deposition method. Overall, the Pd NPs synthesized by the proposed method had better chronoamperometric response compared to Pt/C and Pd/C. Even though the initial decrease in the current density was high for Pd NPs (especially 9 cycles Pd-P), the current density still stabilizes off at a higher level than the Pt/C and Pd/C. Hence, the long term durability of Pd NPs is superior to that of Pt/C and Pd/C.

Next, the durability between amorphous Pd-P and Pd-N₂H₄ is compared. It is observed from Figure 19 that 9 cycles Pd-P stabilizes at a higher current density than both 9 and even 18 cycles of Pd-N₂H₄. Therefore, the amorphous Pd-P is still considered more

durable than crystalline Pd-N₂H₄ at both similar and even greater number of deposition cycles.

Figure 19. Chronoamperometry response of Pd NPs, Pt/C and Pd/C. The measurements were performed in 0.1 M O₂-saturated KOH solution, as per the procedure reported elsewhere (Potential: 0.666 V vs RHE. Rotational speed: 200 rpm).

5. Results and Discussion for Formic Acid Oxidation

5.1 Cyclic Voltammetry Curves for Formic Acid Oxidation

As mentioned previously, the analysis of the electrocatalytic activity for FAO is different from that of ORR. This is because for FAO, no rotation is involved in the measurement as it will conceal the multiple FAO peaks with i_d which makes the observation and evaluation of the FAO peaks inaccurate. Instead, CVs are conducted to obtain the FAO peaks. Figure 18 shows the CV curves for different cycles of Pd-P. Only Pd-P samples were conducted as it showed the most promising results for ORR as well as due to time constraints.

Firstly, the FAO CV curve consists of two scans, a forward (cathodic) as well as a backward (anodic) scan as seen in Figure 20. Both scans produce peaks which are attributed to the formic acid oxidation.^[31, 103] However, only the forward (cathodic) scan is considered in the evaluation of the electrocatalysts because the backward scan allows poisonous intermediates such as carbon monoxide (CO_{ads}) to build up and hence will affect FAO results.^[31] Also, the forward scan is more relevant to real fuel cell situation.^[103] On the other hand, the backward scan is usually omitted because it shows FAO peaks which is a result of the removal of the poisonous CO_{ads} and therefore is not a true reflection of the performance ability of the electrocatalysts.^[31]

As mentioned in the earlier Chapter 2.5, there are two peaks associated with FAO in the forward scan and that the peak at 0 V to 0.3 V (dehydrogenation) is preferred while the peak at 0.45 V is undesired. However, recent publications have shown that achieving only the dehydrogenation pathway is still a problem in FAO.^[31, 44, 103]

Again from Figure 20, it is seen that the amorphous Pd-P synthesized by the proposed electroless deposition method has a significant FAO peaks between 0 V to 0.3 V. This

implies that the FAO undergoes the direct dehydrogenation pathway which is the preferred pathway. Also from Figure 20, the absence of the peak at 0.45 V demonstrates that FAO only occurs through the direct dehydrogenation pathway.

It is also seen in Figure 20 that two discrete peaks are observed in every FAO curve. These two discrete peaks are in agreement with the recent research on the mechanism of FAO. It is demonstrated in those studies that the first peak at the lower potential (0.17 V) corresponds to HCOO^- being oxidized while the peak observed at the higher potential (0.28 V) is the result of bridge-bonded adsorbed formate enhancing HCOO^- oxidation at a higher potential by preventing the adsorption of oxidation of other species on the electrode surface.

Overall, the amorphous Pd-P promotes FAO to undergo the preferred direct dehydrogenation pathway.

Figure 20. (a) Full CV curves for amorphous Pd-P NPs for FAO. (b) Forward scan of amorphous Pd-P NPs for FAO. The number corresponds to the cycles numbers of the stepwise electroless deposition process. The measurements were performed in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M HCOOH}$ solution. Current is normalized by RDE-GC surface area (0.0707 cm^2). Scan rate: 50 mV s^{-1}

5.2 Calculation and Analysis of the Specific and Mass Activity of Palladium Nanoparticles for Formic Acid Oxidation

As mentioned previously, the calculations for i_s and i_m values for the electrocatalysts in FAO are simpler compared to ORR. For FAO, the i_s and i_m values are obtained by normalizing the current values obtained during the experiment with the ECSA and Pd loading respectively following which the highest value is taken as the i_s and i_m values. The ECSA calculations and the Pd loading extraction process are similar to that of ORR. The representative graphs of the different cycles Pd-P and Pd/C for ECSA calculation are shown in Figure 21.

In Figure 22, the SEM images of different deposition cycles of Pd-P NPs are shown. These Pd NPs are seen to be well dispersed regardless of the deposition cycles. The mean size of the Pd NPs are also shown to increase with the number of deposition cycles (6, 9 and 12 cycles were 14, 16, 20 nm respectively).

Figure 23 shows the i_s and i_m values of different cycles of Pd-P for FAO. Also seen in Figure 23, at all the different deposition cycles, the amorphous Pd-P is significantly higher than Pd/C in terms of both i_s and i_m .

Table 7 summarizes maximum i_s and i_m values achieved by the electrocatalysts. Firstly, the maximum i_s values of the electrocatalysts are compared. From Table 7, it is shown that the highest i_s value was achieved by 9 cycles Pd-P (5.7 mA cm^{-2}), followed by 6 cycles Pd-P (4.9 mA cm^{-2}), 12 cycles Pd-P (4.3 mA cm^{-2}) and lastly commercial Pd/C (0.9 mA cm^{-2}). This conclusively shows that based on specific activity, amorphous Pd-P is superior (6.3 times, 5.4 times and 4.7 times respectively) than commercial Pd/C. In fact, 9 cycles Pd-P (5.7 mA cm^{-2}) has the higher catalytic activity compared to those reported in literature.^[31, 44]

From Table 7, it is shown that the P content for 6 cycles Pd-P was 12 at%, 9 cycles Pd-P was 16 at% and 12 cycles was 11 at%. It is interesting to note that the trend of the average P content is reflective of the trend in the i_s values with higher P content yielding greater i_s values. This thesis speculates that with greater P doping, the surface of Pd-P becomes progressively more disorderedly structured which causes the formation of a larger number of low co-ordination active sites.^[80, 104-105] These low co-ordination active sites have been known to increase catalytic activity.^[80, 100, 106-108] The reverse would also be true where less P doping would mean lesser low co-ordination active sites which would cause i_s value to drop. Therefore, this trend observed for the average P content would explain the trend observed in the i_s values.

Again from Table 7, it is shown from 6 deposition cycles to 9 deposition cycles the average P content increases while from 9 deposition cycles to 12 deposition cycles the average P content decreases. It is theorized that this trend could be because there are two types of Pd depositions: (1) seed generation where Pd deposits directly onto the substrate (glassy carbon) and (2) seed growth where Pd subsequently deposits onto Pd that is already deposited.

In the proposed Pd electroless deposition system, the P content of the Pd from seed generation is low while the P content of Pd from seed growth is high, which is consistent with other electroless deposition systems.^[109-110] This can be seen from Table 7 that the 6 deposition cycles sample, which has the lower P content (12 at%) has well dispersed small nanoparticles (mean 14 nm) while the 9 deposition cycles sample has higher P content (16 at%) and larger nanoparticles (mean 16 nm). On the other hand, again from Table 7, the nanoparticles sizes of 12 deposition cycles sample varies widely and contains large nanoparticles (greater than 30 nm) with lots of small nanoparticles (seeds) as well as shown in Figure 21. The highest frequency in the

nanoparticle size distribution of the 12 cycle is at 2 nm. Due to presence of such small nanoparticles (seeds), the average P content dropped down to 11 at%.

Next, the maximum i_m values for the electrocatalysts are compared. As seen from Table 7, the highest i_m value was obtained by 6 cycles Pd-P ($2.9 \text{ mA } \mu\text{g}^{-1}$), followed by 9 cycles Pd-P ($2.0 \text{ mA } \mu\text{g}^{-1}$) and 12 cycles Pd-P ($1.1 \text{ mA } \mu\text{g}^{-1}$) with the lowest being commercial Pd/C ($0.05 \text{ mA } \mu\text{g}^{-1}$). This shows that based on i_m values as well, the amorphous Pd-P at all deposition cycles (58 times, 40 times and 22 times respectively) is superior compared to commercial Pd/C. Furthermore, the maximum i_m value $2.9 \text{ mA } \mu\text{g}^{-1}$ which was observed for 6 cycles Pd-P was higher than those reported in literature.^[31, 44]

It is also noted that in Table 7, there is a decreasing trend in i_m value with increasing deposition cycles. This decreasing trend is the result in increasing coagulation and particle size of the Pd-P NPs. This increase in coagulation and particle size would result in lower i_m values as less Pd is exposed to the electrolyte (wasted Pd).

Figure 21. Full CV of Pd-P at (a) 6 cycles, (b) 9 cycles, (c) 12 cycles and (d) Pd/C conducted in N_2 -saturated solution and swept from -0.2 V to 1.2 V vs Ag/AgCl (KCl sat.). Scan rate: 50 mV s^{-1} . This is a represented graph for each corresponding electrocatalysts.

Figure 22. SEM images (upper) and their corresponding size distribution (lower) of Pd-P for (a) 6 cycles, (b) 9 cycles and (c) 12 cycles of deposition

Figure 23. Forward scan curves for amorphous Pd-P NPs for FAO normalized by (a) ECSA to give specific activity and (b) Pd loading to give mass activity. The number corresponds to the cycles numbers of the stepwise electroless deposition process. The measurements were performed in N_2 -saturated 0.5 M H_2SO_4 + 1 M $HCOOH$ solution. Scan rate: 50 mV s^{-1}

Table 7. Specific, Mass Activities and average P content values for Pd-P and Pd/C at peak potential

Catalysts	Specific Activity (mA cm^{-2})	Mass Activity ($\text{mA } \mu\text{g}^{-1}$)	Average P content (at%)
6 cyc Pd-P	4.9 ± 0.32	2.9 ± 0.6	12
9 cyc Pd-P	5.7 ± 0.74	2.0 ± 0.4	16
12 cyc Pd-P	4.3 ± 0.59	1.1 ± 0.2	11
Pd/C	0.9	0.05	-

5.3 Importance of Amorphous Nature of Palladium Nanoparticles in Formic Acid Oxidation

A similar test (to that of ORR) was conducted to determine if amorphous nature is the key for the superior catalytic activity in FAO.^[17] From Figure 24, it is observed that the i_s of Pd-P drops significantly after the annealing. Furthermore, the ECSA of Pd-P dropped from 3.11 to 0.45 cm^2 which shows the loss of active sites when the Pd-P changed from amorphous to crystalline. These results supports the hypothesis that amorphous nature of Pd-P is key factor in its high catalytic activity.

Figure 24. Specific activity graphs of 6 cycles Pd-P NPs deposited on carbon cloth before and after annealing at 700 °C for 1 hour. The measurements were conducted in N_2 -saturated 0.5 M H_2SO_4 + 1 M HCOOH solution. Scan rate: 50 mV s^{-1} .

5.4 Durability Test of the Palladium Nanoparticles for Formic Acid Oxidation

The durability of Pd-P was compared to that of commercial Pd/C. As seen in Figure 25, it is demonstrated that Pd-P is more durable compared to Pd/C as observed from the gentle slope of the initial current density of Pd-P compared to that of Pd/C which was sharp. The percentage current density of Pd-P were 21 %, 10 % and 7 % of initial current density for 400, 800 and 1200 seconds, while for Pd/C it was 4 %, 3 %, 2 % respectively. This clearly indicates that the drop in percentage current density of Pd-P was always less than Pd/C at each corresponding time interval. This therefore proves that Pd-P is more efficient, durable and has greater poisoning resistance compared to Pd/C.

Figure 25. Chronoamperometry results for both 9 cycles Pd-P and Pd/C. Results were evaluated as a percentage of initial current density. The measurements were performed in N_2 -saturated 0.1 M H_2SO_4 + 0.1 M $HCOOH$ solution at 0.2 V vs Ag/AgCl (sat.).

6. Results and Discussions for Bio-Fuel Cell

6.1 Synthesis of Carbon Nanotubes-Palladium Nanoparticles Composite by Stepwise Electroless Deposition

As mentioned earlier for BFC, the enzyme BOD is the electrocatalyst that is most commonly used for ORR. However, the problem with using BOD is that the electron transfer between the electrode and the enzyme is poor and therefore there is a need to improve this electron transfer rate to improve the catalytic activity.

Recent studies have shown that metal such as Au has been able to improve the BOD electron transfer rate by optimizing the BOD binding conformation to the substrate (via T1 binding) and hence shortening the distance between the Cu active sites and the substrate.^[20-21, 84, 111] However, the synthesis of Au electrodes requires harsh and difficult fabrication process and hence its use is still heavily limited.^[20-21] Pd has shown some degree of success as an alternative for Au with Pd being able to achieve the desired onset potential but lacks in the current output.^[8] Therefore, there is a need for either an alternative metal or simpler fabrication method to achieve improved electron transfer rate and catalytic activity for BOD.

A recent on-going computational study conducted (collaborator) has theorized that crystalline Pd NPs is able to achieve optimal T1 binding of BOD and shorten the distance between Cu active sites and substrate which will improve electron transfer rates. Table 8 shows the computational calculation results from this on-going computational study. It is seen that Pd NPs (T1-orientated $179.1 \text{ kcal mol}^{-1}$, T2/T3-orientated $106.4 \text{ kcal mol}^{-1}$) at all conformations have higher adsorption energies compared to C NPs (T1-orientated $59.3 \text{ kcal mol}^{-1}$, T2/T3-orientated $18.7 \text{ kcal mol}^{-1}$). Furthermore, T1-orientated BOD on Pd NPs had the highest adsorption energy which

would imply that its formation is the most heavily favoured. Next, it is also observed that when comparing T1-orientated binding between Pd and C NPs, the distance between the Cu active sites and Pd NPs (T1-Pd NPs 5.743 Å, T2/T3-Pd NPs 23.237 Å) were much shorter than that of Cu active sites and C NPs (T1-C NPs 6.203 Å, T2/T3-Pd NPs 24.106 Å). This trend is also observed for the suboptimal T2/T3-orientated binding with the distance between Cu active sites and Pd NPs (T1-Pd NPs 51.134 Å, T2/T3-Pd NPs 35.969 Å) being less than that of Cu active sites and C NPs (T1-C NPs 52.698 Å, T2/T3-Pd NPs 37.168 Å). Overall, this computational result would heavily suggest that Pd NPs are able to bind to BOD via the optimal T1 orientation (highest adsorption energy) and thus decrease the distance between Cu active sites and the Pd which in turn increases the electron transfer rate and the catalytic activity.

Based on the above computation results, this thesis aims to fabricate a CNT-Pd-N₂H₄ composite material using the proposed facile stepwise electroless deposition method to enhance BOD ORR catalytic activity. In order to verify the computational results, crystalline Pd-N₂H₄ was used instead of amorphous Pd-P. It is important to note that although Pd is able to undergo ORR, only the enhancement of BOD ORR effect will be analyzed in this thesis.

Table 8. Computational calculation of adsorption energies and distance between Cu active sites and substrate.

Adsorbed Orientation	T1-Substrate Distance (Å)	T2/T3-Substrate Distance (Å)	Adsorption Energy (kcal mol⁻¹)
T1 on Pd NPs	5.743	23.237	-179.1
T2/T3 on Pd NPs	51.134	35.969	-106.4
T1 on C NPs	6.203	24.106	-59.3
T2/T3 on C NPs	52.698	37.168	-18.7

6.2 Characterization of Carbon Nanotubes-Palladium Nanoparticles Composite

The CNT-Pd composite was observed under SEM, STEM and TEM as seen in Figure 26. Figure 26a shows the CNT-Pd composite observed under SEM. From Figure 26a, the Pd NPs are shown to be well dispersed and coated on the CNT. Furthermore, two different types of Pd NPs are identified. The first type of Pd NPs are 12 nm (mean) and can be seen clearly on the SEM image. The second type of Pd NPs however, are very small and only be identified by the slight discolouration on the CNT surface.

In order to view this second type of Pd NPs, STEM was conducted. In Figure 26b, it can be clearly seen that small Pd NPs (mean 3 nm) which appear as white sphere are coating the CNT (grey string-like structure) which further supports the SEM results. In order to view the bigger Pd NPs better, TEM was conducted as well as shown in Figure 26c. It is observed from Figure 26c that the bigger Pd NPs seen in the SEM are actually coagulations of the smaller Pd NPs. Overall, the Pd NPs are judged to be well coated on the CNT.

All in all, the proposed stepwise electroless deposition is demonstrated to be able to successfully coat Pd-N₂H₄ NPs well on the CNT. These Pd NPs comes in two different types mainly the small Pd NPs (3 nm) and the bigger Pd NPs (12 nm) which are made up of the small Pd NPs.

Figure 26. 9 cycles CNT-Pd composite viewed under (a) SEM, (b) STEM, (c) TEM and (d) particle size distribution graph.

6.3 Cyclic Voltammetry of Bilirubin Oxidase with Carbon Nanotube-Palladium Nanoparticles Composite as Support Material

In order to evaluate the effect that the CNT-Pd composite has on enhancing the BOD ORR, full CV scan was conducted. Figure 27a shows the full CV of the BOD with both CNT-Pd composite and only CNT as a support. Firstly, two discrete ORR peaks are observed for CNT-Pd-BOD. The first peak which occurs within the range 0.3 V to 0.6 V can be attributed to ORR from T1-orientated BOD binding and is consistent with literature.^[8, 81] On the other hand, the second peak which occurs within the range of 0 V to 0.2 V is the result of ORR from Pd NPs and is also consistent with literature.^[8]

Therefore, to focus on enhancement of catalytic activity of BOD ORR, only the potential range of 0.3 V to 0.6 V will be used for the analysis as shown in Figure 27b. Furthermore, mass activity of BOD is used as well to eliminate any current increment from different amounts of BOD loading. The BOD loading results were obtained from the UV-Vis spectroscopy. Figure 28 shows the calibration curve as well as the UV-Vis results of the CNT-Pd-BOD and CNT-BOD.

It is seen from Figure 27b that at all potential values, the mass activity of CNT-Pd-BOD was higher than that of CNT-BOD. In fact, the maximum mass activity of CNT-Pd-BOD was $1.01 \text{ mA } \mu\text{g}^{-1}$, which was 1.51 times greater than that of CNT-BOD which was only $0.67 \text{ mA } \mu\text{g}^{-1}$. These results are in agreement with the computational studies and demonstrate that CNT-Pd was a better support material than CNT alone and was able to enhance the ORR capabilities of BOD. This enhancement was due to the optimized T1 binding between Pd and BOD which shorten the distance between

Cu active sites and Pd which in turn increases the electron transfer rate and thus results in a increase in catalytic activity.

Figure 27. ORR polarization curves of CNT-BOD and CNT-Pd-BOD with (a) full CV and (b) zoomed in potential range and mass activity curve. The measurements were conducted in O₂-saturated 0.1 M pH 6.5 PBS. Scan rate: 20 mV s⁻¹

Figure 28. Representative UV-Vis curves of (a) different amounts of BOD for calibration and (b) CNT-BOD and CNT-Pd-BOD. (c) shows the calibration plot obtained from (a) at 420 nm.

6.4 Importance of Palladium Nanoparticles in Enhancing Oxygen Reduction Reaction for Bilirubin Oxidase

As demonstrated earlier, Pd NPs are able to enhance the catalytic activity of BOD ORR. In order to further verify the computational results, the electron transfer rate (k_{cat}) was calculated. To calculate the k_{cat} value, the electron transfer rate equation is used [8, 20, 88].

$$k_{cat} = \frac{j}{n \times F \times r} \quad (11)$$

where j (mA cm^{-2}) is the saturated current density, n is number of electrons involved in the reaction, F (C mol^{-1}) is Farady's constant and r (mol cm^{-2}) is the surface coverage of the enzyme.

Using this equation as well as the experimental results from the previous section (Chapter 6.3), the k_{cat} value for CNT-Pd-BOD was calculated to be 169.4 s^{-1} while CNT-BOD was 99.2 s^{-1} . Therefore, the k_{cat} value for CNT-Pd-BOD was found to be 1.71 times greater compared to that of CNT-BOD. Again, these results are in agreement with that of the computational results. This strongly suggest that Pd is able to direct BOD to bind optimally via T1 binding which decreases the distance between the Cu active sites and Pd which in turn increases the electron transfer rate and the catalytic activity of BOD ORR.

7. Conclusion and Future Work

7.1 Conclusion

In conclusion, this thesis presents stepwise electroless deposition as a facile and superior synthesis method for synthesizing Pd NPs as electrocatalysts. Next, it also showcases the superiority of the synthesized amorphous Pd-P NPs over crystalline Pd-N₂H₄ NPs. Lastly, it demonstrates the effect of Pd NPs in enhancing the catalytic activity of BOD ORR.

The advantages of the proposed stepwise electroless deposition method for the synthesis of Pd NPs as electrocatalysts can be summarized as follows:

1. Synthesis process is remarkably facile and simple. Total time for each deposition cycle is 20 s and no complicated reaction procedures or steps are required. Only one solution containing the reducing agent and another containing the PdCl₂ ions to be reduced.
2. The catalytic, specific and mass activities of the Pd NPs are tunable by simply varying the number of deposition cycles.
3. The electroless deposition process can be used to coat complex shapes and structures which traditional casting method are unable to.
4. Minimal amount of chemical waste is produced.

Overall, the proposed stepwise electroless deposition method has been shown to be an improvement over the traditional methods and is also shown to produce better electrocatalysts compared to those commercially available.

With the benefits of the proposed electroless deposition method explained, the summary of the superiority of the synthesized amorphous Pd-P NPs compared to Pd-N₂H₄ NPs are as follows:

1. Pd-P exhibits higher current density and more positive half-wave potentials compared to Pd-N₂H₄ at similar number of deposition cycles.
2. Pd-P gave a more consistent (higher) number of electrons transferred and specific activity values than Pd-N₂H₄. This shows that Pd-P has more active surface compared to Pd-N₂H₄.
3. Pd-P shows a higher mass activity result at almost every deposition cycles compared to Pd-N₂H₄. The mass activity (2.21 mA μg^{-1}) is also the highest ever reported. This proves that Pd-P is more cost efficient compared to Pd-N₂H₄.

To sum it up, the amorphous Pd-P is superior to the crystalline Pd-N₂H₄ and can be sought to be used in industrial applications.

For FAO, the current advantages of the synthesized amorphous Pd-P has over commercial Pd/C are listed:

1. Pd-P has higher specific (5.7 mAcm⁻²) and mass activity (2.9 mA μg^{-1}) compared to Pd/C (0.9 mAcm⁻² and 0.05 mA μg^{-1}).
2. Pd-P has greater durability and poisoning resistance compared to Pd/C.

For BFC, the current advantages that Pd N₂H₄-CNT composite has over CNT alone are as listed:

1. BOD with Pd N₂H₄-CNT composite as support material is able to achieve significantly higher mass activity compared to CNT alone (1.68 $\mu\text{A}\mu\text{g}^{-1}$ and 0.91 $\mu\text{A}\mu\text{g}^{-1}$ respectively).
2. BOD with Pd N₂H₄-CNT composite as support material has higher electron transfer rate (0.269 s^{-1}) compared to that of CNT only (0.147 s^{-1})

7.2 Future Work

Even though this project has presented a significant advances in both synthesis method as well as the electrocatalysts itself, there are still further areas of interest and improvements which can be made. Similarly, these further research areas can be broken down into 2 different groups, synthesis method and the electrocatalysts.

For the stepwise electroless deposition method, the areas of improvement/new research fronts are listed and explained as follows:

1. Using combinatorial chemistry on the electroless deposition method. Currently, the electroless deposition method is conducted manually. However, using a machine to automate the process will make the handling process even simpler. Also by automating the process, it will make this process more consistent.
2. Varying the deposition timing. So far, the deposition timings has been standardized at 10 s for each dipping process. This timing however, has not been proven to be the optimal timing. Furthermore the human error process time for 10 s dipping is quite high. Hence, further research can be put into achieving optimal amount of dipping time.
3. Varying different experimental conditions. At this time, all the experiments were conducted at room temperature and pressure. Other experimental conditions such as temperature has not been examined and its effect on the deposition and synthesis process is unknown. Therefore, this is an important research front which can be explored.

Next, the areas of improvements for the electrocatalysts itself is stated and explained accordingly:

1. Using different metals. Although Pd itself is cheaper compared to Pt, it is still expensive. An interesting research front would be to use other metals such as Fe or Co NPs, which are significantly cheaper and explore their use in ORR or FAO.
2. Formation of bimetallic electrocatalysts. By using this proposed electroless deposition process, an interesting approach would be to synthesis core/shell structure and form bimetallic NPs. This bimetallic NPs would not only reduce the amount of Pd/Pt load, but still have catalytic ORR or FAO properties.
3. Using support materials. Using support materials such as graphene or carbon is not a new research front. However, by using it with electroless deposition, there might be better dispersion which in turn might improve the catalytic activity of the Pd with graphene or carbon support.
4. Doping of the electrocatalysts. With the current electroless deposition method, it shows the doping of P into the Pd. Although the P does not show any catalytic properties, this might not be true for other doping cases. Hence, exploring the effect of doping of Pd with other elements such as N or B on ORR or FAO would be an interesting research topic.
5. Practical applications. For practical fuel cell applications of the Pd NPs further experimentation of Pd NPs need to be conducted. These includes conducting at air saturated electrolytes, CO/CO₂ poisoning effect and trying a full fuel cell setup.
6. Analysis and overcome of CO₂ poisoning of electrolyte. Try strategies such as increasing the temperature of the fuel cells to overcome the poor solubility of

K_2CO_3 at room temperature, circulating the electrolyte to remove carbonate ions as well as using electrochemical method to reduce the OH^- concentration at the anode which causes the carbonate ions to migrate to the anode and form carbonic acid (preventing the formation of K_2CO_3).

7. In depth analysis of amorphous effect. Use high energy XRD and pair distribution function analysis (PDF) to obtain structure of Pd-P to model to analyze the effect of the increased Pd-Pd bond length.

In the case of BFC which is an on-going work, the following listed experiments will still need to be conducted:

1. Optimize the experimental conditions.
2. Evaluate charge transfer values of the samples to further explore the mechanism of the increment in electron transfer rate.

List of Publication

1. **K. C. Poon**, B. Khezri, Y. Li, R. D. Webster, H. Su, H. Sato, Chemical Communications **2016**, 52, 3556-3559.
2. T. T. Vo Doan, J. Wang, **K. C. Poon**, D. C. L. Tan, B. Khezri, R. D. Webster, H. Su, H. Sato, Angewandte Chemie International Edition **2016**, 55, 6842-6847.
3. **K. C. Poon**, D. C. L. Tan, T. D. T. Vo, B. Khezri, H. Su, R. D. Webster, H. Sato, Journal of the American Chemical Society **2014**, 136, 5217-5220.

References

- [1] M. Falk, Z. Blum, S. Shleev, *Electrochim. Acta* **2012**, 82, 191-202.
- [2] A. Kirubakaran, S. Jain, R. K. Nema, *Renewable and Sustainable Energy Reviews* **2009**, 13, 2430-2440.
- [3] S. J. Peighambaroust, S. Rowshanzamir, M. Amjadi, *Int. J. Hydrogen Energy* **2010**, 35, 9349-9384.
- [4] M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, 104, 4245-4270.
- [5] X.-Z. Yuan, H. Wang, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers* (Ed.: J. Zhang), Springer London, **2008**, pp. 1-87.
- [6] S. Calabrese Barton, J. Gallaway, P. Atanassov, *Chem. Rev.* **2004**, 104, 4867-4886.
- [7] J. A. Cracknell, K. A. Vincent, F. A. Armstrong, *Chem. Rev.* **2008**, 108, 2439-2461.
- [8] D. Wen, W. Liu, A.-K. Herrmann, A. Eychmüller, *Chemistry – A European Journal* **2014**, 20, 4380-4385.
- [9] M. Southcott, K. MacVittie, J. Halamek, L. Halamkova, W. D. Jemison, R. Lobel, E. Katz, *PCCP* **2013**, 15, 6278-6283.
- [10] M. Rasmussen, R. E. Ritzmann, I. Lee, A. J. Pollack, D. Scherson, *J. Am. Chem. Soc.* **2012**, 134, 1458-1460.
- [11] A. de Poulpiquet, A. Ciaccafava, E. Lojou, *Electrochim. Acta* **2014**, 126, 104-114.
- [12] F. Davis, S. P. J. Higson, *Biosens. Bioelectron.* **2007**, 22, 1224-1235.
- [13] C. Song, J. Zhang, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers* (Ed.: J. Zhang), Springer London, **2008**, pp. 89-134.
- [14] A. A. Gewirth, M. S. Thorum, *Inorg. Chem.* **2010**, 49, 3557-3566.
- [15] M. Oezaslan, F. Hasché, P. Strasser, *J. Electrochem. Soc.* **2012**, 159, B444-B454.
- [16] K. P. Gong, F. Du, Z. H. Xia, M. Durstock, L. M. Dai, *Science* **2009**, 323, 760-764.
- [17] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Applied Catalysis B: Environmental* **2005**, 56, 9-35.
- [18] S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, 412, 169-172.
- [19] E. Katz, K. MacVittie, *Energy & Environmental Science* **2013**, 6, 2791-2803.
- [20] C. Gutierrez-Sanchez, A. Ciaccafava, P. Y. Blanchard, K. Monsalve, M. T. Giudici-Orticoni, S. Lecomte, E. Lojou, *ACS Catalysis* **2016**, 6, 5482-5492.
- [21] P. Ramírez, N. Mano, R. Andreu, T. Ruzgas, A. Heller, L. Gorton, S. Shleev, *Biochimica et Biophysica Acta (BBA) - Bioenergetics* **2008**, 1777, 1364-1369.
- [22] B. C. H. Steele, A. Heinzl, *Nature* **2001**, 414, 345-352.
- [23] M. A. Laguna-Bercero, *J. Power Sources* **2012**, 203, 4-16.
- [24] J. M. E. Harper, C. Cabral, P. C. Andricacos, L. Gignac, I. C. Noyan, K. P. Rodbell, C. K. Hu, *J. Appl. Phys.* **1999**, 86, 2516-2525.
- [25] G. Merle, M. Wessling, K. Nijmeijer, *Journal of Membrane Science* **2011**, 377, 1-35.
- [26] T. E. Springer, T. A. Zawodzinski, S. Gottesfeld, *J. Electrochem. Soc.* **1991**, 138, 2334-2342.
- [27] H. Li, K. Lee, J. Zhang, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers* (Ed.: J. Zhang), Springer London, **2008**, pp. 135-164.

- [28] R. C. T. Slade, J. P. Kizewski, S. D. Poynton, R. Zeng, J. R. Varcoe, in *Fuel Cells: Selected Entries from the Encyclopedia of Sustainability Science and Technology* (Ed.: K.-D. Kreuer), Springer New York, New York, NY, **2013**, pp. 9-29.
- [29] B. Liang, X. Guo, L. Fang, Y. Hu, G. Yang, Q. Zhu, J. Wei, X. Ye, *Electrochem. Commun.* **2015**, *50*, 1-5.
- [30] J. Zhang, *PEM fuel cell electrocatalysts and catalyst layers: fundamentals and applications*, Springer, **2008**.
- [31] R. Ojani, Z. Abkar, E. Hasheminejad, J. B. Raoof, *Int. J. Hydrogen Energy* **2014**, *39*, 7788-7797.
- [32] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley: New York, **2001**.
- [33] A. Kongkanand, G. Girishkumar, S. Kuwabata, P. Kamat, *Langmuir* **2006**, *22*, 2392-2396.
- [34] V. Nallathambi, J.-W. Lee, S. Kumaraguru, G. Wu, B. Popov, *J. Power Sources* **2008**, *183*, 34-42.
- [35] M. H. Seo, S. M. Choi, H. J. Kim, W. B. Kim, *Electrochem. Commun.* **2011**, *13*, 182-185.
- [36] B. Lim, M. Jiang, P. H. C. Camargo, E. Cho, J. Tao, Y. Xia, X. Lu, Y. Zhu, *Science* **2009**, *324*, 1302-1305.
- [37] N. M. Markovic, R. R. Adzic, N. M. Marković, R. R. Adžić, B. D. Cahan, E. B. Yeager, *J. Electroanal. Chem.* **1994**, *377*, 249-259.
- [38] D. Higgins, H. Tao, R. Hsu, Z. Chen, *The journal of physical chemistry. C* **2009**, *113*, 21008-21013.
- [39] U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, *J. Electroanal. Chem.* **2001**, *495*, 134-145.
- [40] S. Guo, S. Zhang, L. Wu, S. Sun, *Angew. Chem. Int. Ed.* **2012**, *51*, 11770-11773.
- [41] C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, *J. Am. Chem. Soc.* **2007**, *129*, 6974-6975.
- [42] S. Koh, P. Strasser, *J. Am. Chem. Soc.* **2007**, *129*, 12624-12625.
- [43] T. Chierchie, C. Mayer, W. J. Lorenz, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1982**, *135*, 211-220.
- [44] J. F. Chang, L. G. Feng, C. P. Liu, W. Xing, X. L. Hu, *Angewandte Chemie-International Edition* **2014**, *53*, 122-126.
- [45] M. A. Matin, J. H. Jang, Y. U. Kwon, *J. Power Sources* **2014**, *262*, 356-363.
- [46] E. Britannica, *Platinum*, Encyclopædia Britannica Inc, **2012**.
- [47] P. J. Loferski, *2010 Minerals Yearbook; Platinum-group metals*, USGS Mineral Resources Program, **2011**.
- [48] J. C. Ely, C. R. Neal, C. F. Kulpa, M. A. Schneegurt, J. A. Seidler, J. C. Jain, *Environmental Science & Technology* **2001**, *35*, 3816-3822.
- [49] J. D. Bracken, *J. Chem. Educ.* **1999**, *76*, 475.
- [50] N. R. Elezovic, B. M. Babic, V. R. Radmilovic, L. M. Vracar, N. V. Krstajic, *Electrochim. Acta* **2011**, *56*, 9020-9026.
- [51] I. S. Park, K. S. Lee, J. H. Choi, H. Y. Park, Y. E. Sung, *Journal of Physical Chemistry C* **2007**, *111*, 19126-19133.
- [52] Z. Chen, M. Waje, W. Li, Y. Yan, *Angew. Chem. Int. Ed.* **2007**, *46*, 4060-4063.
- [53] M. C. Orilall, F. Matsumoto, Q. Zhou, H. Sai, H. D. Abruña, F. J. DiSalvo, U. Wiesner, *J. Am. Chem. Soc.* **2009**, *131*, 9389-9395.
- [54] Z. Peng, H. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 7542-7543.

- [55] G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* **2011**, 332, 443-447.
- [56] D. Ciuparu, M. Lyubovsky, E. Altman, L. Pfefferle, A. Datye, *Catalysis reviews. Science and engineering* **2002**, 44, 593-649.
- [57] InvestmentMine, Vol. 2017, **2017**.
- [58] L. Jiang, A. Hsu, D. Chu, R. Chen, *J. Electrochem. Soc.* **2009**, 156, B643-B649.
- [59] S. Mentus, A. Abu Rabi, D. Jašin, *Electrochim. Acta* **2012**, 69, 174-180.
- [60] A. B. Papandrew, C. R. I. Chisholm, S. K. Zecevic, G. M. Veith, T. A. Zawodzinski, *J. Electrochem. Soc.* **2013**, 160, F175-F182.
- [61] S. Yang, J. Dong, Z. Yao, C. Shen, X. Shi, Y. Tian, S. Lin, X. Zhang, *Scientific Reports* **2014**, 4, 4501.
- [62] H. Erikson, A. Sarapuu, N. Alexeyeva, K. Tammeveski, J. Solla-Gullón, J. M. Feliu, *Electrochim. Acta* **2012**, 59, 329-335.
- [63] S. Maheswari, P. Sridhar, S. Pitchumani, *Electrochem. Commun.* **2013**, 26, 97-100.
- [64] M. Neergat, V. Gunasekar, R. Rahul, *J. Electroanal. Chem.* **2011**, 658, 25-32.
- [65] A. Budniok, J. Kupka, *Electrochim. Acta* **1989**, 34, 871-873.
- [66] E. Antolini, *Energy & Environmental Science* **2009**, 2, 915-931.
- [67] A. Anastasopoulos, J. C. Davies, L. Hannah, B. E. Hayden, C. E. Lee, C. Milhano, C. Mormiche, L. Offin, *ChemSusChem* **2013**, 6, 1973-1982.
- [68] M. Shao, T. Yu, J. H. Odell, M. Jin, Y. Xia, *Chem. Commun.* **2011**, 47, 6566-6568.
- [69] L. Xiao, L. Zhuang, Y. Liu, J. Lu, H. c. D. Abruña, *J. Am. Chem. Soc.* **2008**, 131, 602-608.
- [70] J. Yang, C. G. Tian, L. Wang, H. G. Fu, *J. Mater. Chem.* **2011**, 21, 3384-3390.
- [71] R. Carrera-Cerritos, V. Baglio, A. S. Aricò, J. Ledesma-García, M. F. Sgroi, D. Pullini, A. J. Pruna, D. B. Mataix, R. Fuentes-Ramírez, L. G. Arriaga, *Applied Catalysis B: Environmental* **2014**, 144, 554-560.
- [72] M. H. Seo, S. M. Choi, J. K. Seo, S. H. Noh, W. B. Kim, B. Han, *Applied Catalysis B: Environmental* **2013**, 129, 163-171.
- [73] J. J. Podestá, R. C. V. Piatti, *Int. J. Hydrogen Energy* **1997**, 22, 753-758.
- [74] A. N. Correia, L. H. Mascaró, S. A. S. Machado, L. A. Avaca, *Journal of the Brazilian Chemical Society* **1999**, 10, 478-482.
- [75] P. H. Matter, L. Zhang, U. S. Ozkan, *J. Catal.* **2006**, 239, 83-96.
- [76] A. Kuzume, E. Herrero, J. M. Feliu, *J. Electroanal. Chem.* **2007**, 599, 333-343.
- [77] M. D. Maciá, J. M. Campiña, E. Herrero, J. M. Feliu, *J. Electroanal. Chem.* **2004**, 564, 141-150.
- [78] F. Cheng, Y. Su, J. Liang, Z. Tao, J. Chen, *Chem. Mater.* **2009**, 22, 898-905.
- [79] J. Yang, J. J. Xu, *Electrochem. Commun.* **2003**, 5, 306-311.
- [80] R. F. Wang, H. Wang, X. L. Wang, S. J. Liao, V. Linkov, S. Ji, *Int. J. Hydrogen Energy* **2013**, 38, 13125-13131.
- [81] G. Gupta, C. Lau, V. Rajendran, F. Colon, B. Branch, D. Ivniński, P. Atanassov, *Electrochem. Commun.* **2011**, 13, 247-249.
- [82] M. J. Cooney, V. Svoboda, C. Lau, G. Martin, S. D. Minter, *Energy & Environmental Science* **2008**, 1, 320-337.
- [83] C. F. Blanford, R. S. Heath, F. A. Armstrong, *Chem. Commun.* **2007**, 1710-1712.
- [84] L. dos Santos, V. Climent, C. F. Blanford, F. A. Armstrong, *PCCP* **2010**, 12, 13962-13974.
- [85] J. Wang, M. Li, Z. Shi, N. Li, Z. Gu, *Anal. Chem.* **2002**, 74, 1993-1997.

- [86] W. Putzbach, N. Ronkainen, *Sensors* **2013**, *13*, 4811.
- [87] L. Qu, Y. Liu, J.-B. Baek, L. Dai, *ACS Nano* **2010**, *4*, 1321-1326.
- [88] A. Trifonov, K. Herkendell, R. Tel-Vered, O. Yehezkeli, M. Woerner, I. Willner, *ACS Nano* **2013**, *7*, 11358-11368.
- [89] U. Erb, A. F. Zimmerman, D. G. Clark, K. T. Aust, *Mater. Lett.* **2002**, *52*, 85-90.
- [90] Y. Lee, A. Loew, S. Sun, *Chem. Mater.* **2009**, *22*, 755-761.
- [91] D. Li, C. Wang, D. Tripkovic, S. Sun, N. M. Markovic, V. R. Stamenkovic, *ACS Catalysis* **2012**, *2*, 1358-1362.
- [92] K. Niu, B. Yang, J. Cui, J. Jin, X. Fu, Q. Zhao, J. Zhang, *Journal of Power Sources* **2013**, *243*, 65-71.
- [93] W. Yang, T.-P. Feller, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 206-209.
- [94] Z. Cui, R. G. Burns, F. J. DiSalvo, *Chem. Mater.* **2013**, *25*, 3782-3784.
- [95] H.-Q. Dong, Y.-Y. Chen, M. Han, S.-L. Li, J. Zhang, J.-S. Li, Y.-Q. Lan, Z.-H. Dai, J.-C. Bao, *Journal of Materials Chemistry A* **2014**, *2*, 1272-1276.
- [96] C. Han, J. Wang, Y. Gong, X. Xu, H. Li, Y. Wang, *Journal of Materials Chemistry A* **2014**, *2*, 605-609.
- [97] M. S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* **1992**, *22*, 1-7.
- [98] X. Sun, R. Li, D. Villers, J. P. Dodelet, S. Désilets, *Chem. Phys. Lett.* **2003**, *379*, 99-104.
- [99] L. O. Gullman, *Journal of the Less Common Metals* **1966**, *11*, 157-167.
- [100] J.-S. Lee, G. S. Park, H. I. Lee, S. T. Kim, R. Cao, M. Liu, J. Cho, *Nano Lett.* **2011**, *11*, 5362-5366.
- [101] F. Cheng, J. Shen, B. Peng, Y. Pan, Z. Tao, J. Chen, *Nat Chem* **2011**, *3*, 79-84.
- [102] T. T. Vo Doan, J. Wang, K. C. Poon, D. C. L. Tan, B. Khezri, R. D. Webster, H. Su, H. Sato, *Angew. Chem. Int. Ed.* **2016**, *55*, 6842-6847.
- [103] N. Kristian, Y. S. Yan, X. Wang, *Chem. Commun.* **2008**, 353-355.
- [104] K. C. Poon, B. Khezri, Y. Li, R. D. Webster, H. Su, H. Sato, *Chem. Commun.* **2016**, *52*, 3556-3559.
- [105] K. C. Poon, D. C. L. Tan, T. D. T. Vo, B. Khezri, H. Su, R. D. Webster, H. Sato, *J. Am. Chem. Soc.* **2014**, *136*, 5217-5220.
- [106] Y. Wang, S.-I. Choi, X. Zhao, S. Xie, H.-C. Peng, M. Chi, C. Z. Huang, Y. Xia, *Adv. Funct. Mater.* **2014**, *24*, 131-139.
- [107] Y. Xia, J. Liu, W. Huang, Z. Li, *Electrochim. Acta* **2012**, *70*, 304-312.
- [108] N. Arjona, M. Guerra-Balcazar, F. M. Cuevas-Muniz, L. Alvarez-Contreras, J. Ledesma-Garcia, L. G. Arriaga, *Rsc Advances* **2013**, *3*, 15727-15733.
- [109] Z. Liu, W. Gao, *Surf. Coat. Technol.* **2006**, *200*, 3553-3560.
- [110] N. El Mahallawy, A. Bakkar, M. Shoeib, H. Palkowski, V. Neubert, *Surf. Coat. Technol.* **2008**, *202*, 5151-5157.
- [111] I. Matanovic, S. Babanova, M. S. Chavez, P. Atanasov, *J. Phys. Chem. B* **2016**, *120*, 3634-3641.