INVESTIGATION OF TERNARY CATALYSTS AS ANODE CATALYSTS FOR DIRECT METHANOL FUEL CELL

By

NURUDEEN ADEWUNMI ADEBARE

BSc Industrial Chemistry (University of Lagos, Nigeria), MSc Chemistry (University of Lagos, Nigeria)

A thesis submitted in partial fulfilment of the requirements for the degree of

PHILOSOPHIAE DOCTOR

In the

Department of Chemistry

University of the Western Cape, South Africa

Supervisor: Professor Lindiwe E. Khotseng

January 2023

ABSTRACT

Due to the depletion of fossil fuels and the rising environmental pollution, fuel cells have generated a lot of interest as renewable power sources for mobile, stationary and portable electronic gadgets. The direct methanol fuel cell (DMFC) is a promising alternative energy source for portable devices. However, for DMFC to be used as an alternative energy source for the aforementioned devices at an affordable cost is challenging, hence the need for research and development in DMFCs. With pure platinum being used as an anode catalyst of a DMFC, carbon monoxide formed poisonous catalytic sites thereby decreasing the life span of the catalyst if the CO is not removed. Research has shown that the bi-functional mechanism of a platinum-ruthenium catalyst is best because methanol dehydrogenates well on platinum and water dehydrogenation is best facilitated on ruthenium. It is also reported that the addition of certain transition metals to a bimetallic platinum-ruthenium catalyst can make the catalyst more effective and increase the life span even further. My research has attempted to improve catalyst performance for DMFCs by synthesizing ternary catalysts for improved electro-activities. Firstly, by using four catalyst preparation methods namely, Impregnation, polyol, modified polyol and microwave assisted modified polyol processes to synthesize binary catalyst PtRu supported on multiwalled carbon nanotubes (MWCNT) and finally using the best (of the four catalyst preparation methods (microwave assisted modified polyol method) to synthesize the ternary catalysts PtRuIr/MWCNT, PtRuMo/MWCNT and PtRuW/MWCNT. The binary PtRu/MWCNT were also heat treated at higher temperature of 250^0C, 350^0C and 450^0C for optimisation and compared with the performance of the best binary PtRu/MWCNT catalyst synthesized by the four synthesis methods.

The synthesized binary catalysts, ternary catalysts and heat-treated catalysts were characterized by electrochemical methods including cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry for electroactivity and electroactive surface area, reaction kinetics and stability of the electrocatalysts respectively. Energy dispersive X-ray Spectroscopy, EDS was used for elemental analysis, X-ray diffraction, XRD for structural properties and high-resolution transmission electron microscopy, HR-TEM for morphological characterization and particle sizes determination. It was noted that in all the catalysts, the heat treatment had a positive effect on the anodic methanol oxidation reaction, MOR. PtRu/MWCNT heat treated at 450 °C performed better than other heat treated electrocatalysts. It showed better performance in conductivity with charge transfer resistances of 0.151kΩ. as compared to PtRu/MWCNT catalysts heat treated at 250^0C and 350^0C with charge transfer resistances of 11.31kΩ and 2.040kΩ respectively.

Ternary catalyst PtRuMo/MWCNT proved to be the most active anode catalyst towards methanol oxidation producing the highest current density, lowest onset potential and superiority in electroactivity and conductivity with its highest electroactive catalyst surface area of 180m^2/g and lowest charge transfer resistance value of 1.045 kΩ as compared to other ternary catalysts and commercial PtRu/C catalysts which was used as the baseline while PtRuW/MWNT proved to be the most stable catalyst as compared to other ternary catalysts followed by the PtRu/C commercial catalyst.

The HR-TEM revealed the particle sizes in the range of 1.20-4.33 nm while XRD showed the crystalline sizes ranging from 1.36- 4.96nm for the ternary catalysts. The XRD results indicated that PtRu/MWCNT, PtRuW/MWCNT, PtRuMo/MWCNT and PtRuIr/MWCNT electrocatalysts presented typical face-centred cubic crystallographic structures, the structure characteristic for pure Pt. Commercial PtRu/C and PtRuW/MWCNT had mass activities of 16.34A/g and 5.69A/g respectively as compared to PtRuIr/MWCNT and PtRuMo/MWCNT which demonstrated better electrocatalytic activity towards methanol oxidation of higher mass activities of 22.68A/g and 51.79A/g respectively.

LIST OF ABBREVIATIONS

CV:	Cyclic Voltammetry
DAFCs:	Direct Alcohol Fuel Cells
DMFC:	Direct Methanol Fuel Cells
EG:	Ethylene glycol
EIS:	Electrochemical Impedance Spectroscopy
EDS:	Energy Dispersive Spectroscopy
FTIR:	Fourier Transform Infra-Red Spectroscopy
HRTEM:	High Resolution Transmission Electron Microscopy
MWCNTs:	Multi Walled Carbon nanotubes
PtRu/MWCNT	Platinum Ruthenium on multi walled carbon nanotubes
PtRuIr/MWCNT	Platinum Ruthenium Iridium on multi walled carbon nanotubes
PtRuMo/MWCNT	Platinum Ruthenium Molybdenum on multi walled carbon nanotubes
Rct	Charge transfer Resistance
XRD	X-ray Diffraction Spectroscopy

DECLARATION

I hereby declare that “**Investigation of ternary catalysts as anode catalysts for direct methanol fuel cell**” is my own work; that it has not been previously submitted for any degree or examination in any other university or higher education; and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Nurudeen Adebare Adewunmi **January, 2023.**

Signature:

DEDICATION

This dissertation is dedicated to

Allah, the custodian of Knowledge.

My Caring Parents

Mrs Rahmat Adebare, Late Mrs Hafsah Adebare (step mother) &Late Mr Mufutau Adebare

My darling Jewels

My wife, Khadijah Oritoke Jumah-Adebare and Children.

ACKNOWLEDGEMENTS

"Are those who know and those who do not alike? Only men of understanding are mindful" (Q39:9).

If not for the opportunity of creation, I wouldn't have made it to the planet Earth to appreciate the elemental compositions of matter and their usefulness. All praises and adorations are due to the Lord of the Worlds, Allah.

Professor Lindiwe Eudora Khotseng has my undying gratitude and appreciation for her exceptional supervision, meticulous direction, kindness, patience, constructive critics, time-to-time words of encouragement, continual availability, and financial support during my Ph.D. studies. I am deeply grateful and pray that the almighty God continues to bless and nourish you with wisdom. It has been a lifetime opportunity to contribute knowledge in fuel cell technology under your tutelage. Your acceptance to supervise my Ph.D. research work is the reason I found my humble self at UWC, where students are endowed with the required knowledge to transform hope into action. The reason this fuel cell research worked out and my outstanding performance at the MIOMeT laboratory at the University of Valladolid, Spain having got the scholarship offer for the Erasmus+ KA 107 student exchange mobility. Many thanks, my dear Professor.

To him, he believed in his only son, Alowonle, my late father. I pray Almighty Allah to forgive you, overlook your shortcomings, and admit you into his paradise. Your all-time motivation lingers in me when the waves are turbulent. To my late stepmother, your Nuru keeps pushing to make it to the zenith of accomplishment, I pray Allah rewards you with the Garden of Eden for your care. To my dear mother, I thank you for your prayers and love. May you live long with sound health and affluence.

My heartfelt gratitude goes out to my siblings, Mrs. Isimot Adenike Ibikunle (nee Adebare), Mrs. Surajah Titilayo Akinwunmi (nee Adebare), and late Nimota Jokotade Adebare for your love, support, prayers, calls, and understanding. I love you all.

I sincerely appreciate my father-in-law, mother-in-law, sister, and brother-in-laws Mr. Kamorudeen Ishola Jimoh, Mrs Abeni Jimoh, Mrs Sherifat Akinfenwa, Mrs Fatimat, and Mr Tunde Jumah for their unquantifiable love, messages, calls, care, understanding and continuous support.

To my glittering jewel, my darling wife, Khadijah Ibilola Oritoke Jumah-Adebare that made my coming to UWC, South Africa a reality accepting to shoulder the responsibility of taking care of the entire household by His grace, the difficult task to care of our lovely children, the wise men in the palace, Abdullah Adekunmi Adebare, Muhammad Adeola Adebare, Khabbab

Adetola Adebare, Anas Adedamola Adebare, Yusuf Ademola Adebare, Talhah Adeyinka Adebare and my princess, Maryam Adesola Adebare I appreciate this highly rewarding sacrifice. I acknowledge your unquantifiable love, messages, calls, care, understanding, and continuous support. I love you all from the depth of my heart.

To my ever-supportive colleagues and friends at the energy and nanomaterials laboratory especially Jerome Akindeji Sabejeje. I say it has been awesome to work with you guys, many thanks for your support and encouragement. I see us becoming great researchers of high repute in the future.

I want to especially appreciate Dr. Sodiq Tolulope Yussuf, Dr. Kazeem Badmus, and others for their academic, moral, and spiritual support while studying for my Ph.D. degree.

In this vein, I sincerely appreciate Dr. Kazeem Badmus and Dr. Khadijah Dauda for being the middlemen between me and my supervisor making it a possibility for me to have PhD supervisor here at UWC. May Allah in His infinite mercy overlook the shortcomings of late Dr A/Afeez Jaiyeola for accommodating me in his room for a month before I got my room at HPR. May Allah continue to reward you all abundantly.

I appreciate my brothers in faith calling attention to be focussed on my research and be spiritually conscious at all times. I say Jazakumullahu Khaira to all of you.

My profound appreciation to HySA Systems for sponsoring my Ph.D. program through the intervention of my supervisor, Professor Lindiwe Eudora Khotseng. The financial assistance made my day here at UWC. I am equally grateful to the South African National Zakah Fund (SANZAF) for its moral, spiritual, and financial support. May Allah continue to strengthen your organization.

Many thanks to the University of the Western Cape, International relation Office, Erasmus+ University of Valladolid, and Erasmus program of the European Union for being selected as a beneficiary in the Erasmus+ KA 107 student exchange mobility program at the University of Valladolid between September 23, 2021, and February 22, 2022. I appreciate my host Supervisors Professor Celedonio Alvarez and Professor Daniel Miguel San Jose and Nerea Alvarez for an awesome co-supervision. I thank Professor Fernando and other colleagues in the MIOMET laboratory for their hospitality and for making my stay a worthwhile experience.

LIST OF PUBLICATIONS

Adebare Nurudeen Adewunmi, Sabejeje Akindeji Jerome, Su Huaneng and Khotseng Lindiwe Eudora. Investigation of Synthesis Methods for Improved Platinum-Ruthenium Nanoparticles Supported on Multi-Walled Carbon Nanotube Electrocatalysts for Direct Methanol Fuel Cells. In: Khotseng, L. E, editor. Electrocatalysis and Electrocatalysts for a Cleaner Environment - Fundamentals and Applications [Working Title] [Internet]. London: IntechOpen; 2022 [cited 2022 Jun 06]. Available from: https://www.intechopen.com/online-first/81502 doi: 10.5772/intechopen.104541

Adewunmi, A. N. , Huaneng, S. , Eudora, K. L. Investigation of Ternary Catalysts Prepared by Microwave assisted modified polyol method as Anode Catalysts For Direct Methanol Fuel Cell (Submitted)

Adebare, N. A & Khotseng, L.E. Electrochemical investigation of heat treated PtRu

nanoparticles prepared by modified polyol method for direct methanol fuel cell application(submitted).

Akindeji Jerome Sabejeje *, **Nurudeen Adewumi Adebare**, Huaneng Su, Lindiwe Khotseng Development of carbonaceous support materials for direct methanol fuel cell.(In Preparation)

CONFERENCES AND WORKSHOPS

CONFERENCES

Adebare Nurudeen Adewunmi, Akindeji Jerome Sabejeje, Khotseng Lindiwe, E. 70th Annual Meeting of the International Society of Electrochemistry held on the 4-9 August 2019 at the International conference Centre Durban, South Africa with poster presentation titled Investigation of Ternary catalysts as anode catalysts for direct methanol fuel cells.

Adebare Nurudeen Adewunmi , Akindeji Jerome Sabejeje, Khotseng Lindiwe, 71st Annual Meeting of the International Society of Electrochemistry held online from 31st August-4th September 2020 with the poster presentation titled electrochemical investigation of heat treated PtRu nanoparticles prepared by modified polyol method at varying pH for direct methanol fuel cell application.

Adebare Nurudeen Adewunmi , Akindeji Jerome Sabejeje, Khotseng Lindiwe, 72nd Annual meeting or the international Society of Electrochemistry, 29 August- 3 September 2021,(Poster and short Oral Presentation (5minutes) Titled: Investigation of PtRu and PtRu(X) nanoparticles prepared by microwave assisted modified polyol method for direct methanol fuel cell application.

Adebare Nurudeen Adewunmi, Akindeji Jerome Sabejeje, Khotseng Lindiwe,.National Young Chemists' Symposium 2021. 8-9 July, 2021(Poster presentation) Titled: Investigation of ternary catalysts PtRuMo and PtRuIr prepared by microwave assisted modified polyol method for direct methanol fuel cell

Adebare Nurudeen Adewunmi , Akindeji Jerome Sabejeje, Khotseng Lindiwe; 73rd Annual meeting or the international Society of Electrochemistry, 12 September -14 September, 2022(Oral Presentation titled; Electrochemical investigation of heat treated binary PtRu nanoparticles at optimum temperature and ternary PtRuMo nanoparticles prepared by microwave assisted modified polyol method for direct methanol fuel cell application.

The 73rd Annual Meeting (Conference) of the International Society of Electrochemistry (online), 12th – 16th September 2022.

Sabejeje A. J; Khotseng L. E. and Adebare N. A. (2022): The physico-chemical study of supports materials on binary catalysts for direct methanol fuel cells.

The 72nd Annual Meeting (Conference) of the International Society of Electrochemistry held in Jeju Korea between 29th August – 3rd September, 2021.

Sabejeje A. J. Khotseng L. E. and Adebare N. A. (2021): Effect of hybrid support materials on electrocatalysts for direct methanol fuel cells.

The 71st Annual Meeting (Conference) of the International Society of Electrochemistry held in Belgrade, Serbia between 30th August – 4th September, 2020.

Sabejeje A. J. and Adebare N. A. (2020): Development of Graphene-Based Supports for direct methanol fuel cells.

The 70th Annual Meeting (Conference) of the International Society of Electrochemistry held at Inkosi Albert Luthuli International Convention Centre, Durban, South Africa between 4th – 9th August, 2019.

Sabejeje A. J; Khotseng L. and Adebare N. A. (2019): Development of Carbon Supports for direct methanol fuel cells.

Young Chemists Symposium held at UCT 8-9 July, 2021 (Poster presentation)

Sabejeje A. J; Adebare N. A. and Khotseng L. E. (2021): Development of carbonaceous support for direct methanol fuel cells.

Young Chemists Symposium held at Stellenbosch 9th September, 2022 (Poster presentation)

Sabejeje A. J; Adebare N. A. and Khotseng L. E. (2021): Effects of Hybrid Support Materials on Electrocatalyst for Direct Methanol Fuel Cell.

WORKSHOPS

- **Adebare Nurudeen Adewunmi** , Joint international Workshop on South Africa and China NRF/MOST project 2020-2021(Oral Presentation) September 29, 2021; Titled: Investigation of Ternary Catalysts prepared by microwave assisted modified polyol method as anode catalysts for direct methanol fuel cell
- Workshop on guide to Publishing research finding vis-a- vis writing, reviewing and ethical issues presented by Mary-Ann Zimmerman, a senior Publisher at Elsevier held on June 1ST 2020 (Webinar).
- Unique workshop for advanced and mid-career researchers on books publishing by Stacy Masucci (Over 20 years of experience in Publishing) held on June 3rd 2020(Webinar)
- The 5th South African Nanoscience and Nanotechnology Summer School held at Devonvale Golf and Wine Estate, Stellenbosch on 25-29 November 2019.
- Oral Presentation at the Materials to Membrane Electrode Assembly's seminar held on the 31st of July 2019 at the University of Cape Town.
- The 2019 Western Cape Young Chemists' Symposium on the 17th May 2019 held at Cape Peninsula University of University Bellville Campus. South Africa.
- Fifth world congress on risk development and resilience SETAC Africa 9th Biennial conference held at Cape Town international Convection Center Cape Town, South Africa on the 6-8 May 2019
- Professor Andrew Crouch honorary electrochemistry symposium at Durbanville South Africa 2018; Professor Andrew Crouch is a former head of chemical Science department, UWC.
- Professor Brian O'Connell Fellowship programme; Public lecture by Prof Omowunmi Sadik founding Director of the Center for Research in Advanced Sensing Technologies and Environmental (CREATES) at the State University of New York (SUNY) at Binghamton. March 28, 2018.

RESEARCH VISIT

ERASMUS+ KA107 student exchange mobility program at the University of Valladolid, Spain, from **23/09/2021 - 22/02/2022** carrying out activities in the programme of: **Doctorate in Chemistry: Synthesis Chemistry, Catalysis and Advanced Materials.**

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO ENERGY SOURCES

Fuel cells are highly efficient energy-converting devices with low or zero emission. The global high-energy demands, environmental pollution cum fossil fuel depletions grossly contribute to the far-reaching interest of researchers in DMFC in recent decades. Production and storage of hydrogen and its transportation are the major challenges in addition to cost and durability issues for hydrogen gas-fed fuel cells with state-of-the-art technology. Arico et al [1] and S. Wasmus et al [2] stated that direct methanol fuel cells (DMFCs), using liquid and renewable methanol fuel, have been a favorable option in terms of feed strategies and fuel usage. Direct methanol fuel cells use a liquid methanol fuel that is easily stored and transported and simplify the fuel cell system compared to hydrogen fuel cells having a reforming unit, or low capacity in the hydrogen storage tank.

The success of fuel cell technology largely depends on the membrane and the electro-catalyst. These two key materials are major challenges faced in DMFCs, including; (1) slow anode kinetics which can only be overcome by developing new anode catalysts, and (2) methanol crossover which can only be overcome by developing new membranes and novel cathode catalysts. Performance, including activity, reliability and durability and cost reduction are two major challenges in developing new DMFC anode catalysts. The exploration of new catalyst materials including noble and non-noble metals is necessary to improve DMFC anode catalyst performance. Alloying strategy is one of the researches and development directions. In proton exchange membrane fuel cells including DMFCs nanoparticle supported catalysts are believed to be the most promising materials for electrocatalysis [22]. Another R&D direction is the reduction of catalyst loading through increasing Pt utilization. The cost reduction, DMFC anode catalyst loadings must reduce from the present 2.0–8.0 mg cm^{-2} to a level of <1.0 mg cm^{-2}, depending on applications for early DMFC commercialization [3]. Nanoparticle-supporting strategies and alloying could dramatically reduce the Pt content in the catalysts without performance compromise. The development of a non-noble catalyst is the other approach for electrocatalyst cost reduction but currently, its feasibility is not attained. A more thorough exploration is needed in this area. This research focuses on the investigation of catalyst preparation methods, heat treatment for optimization, and production of multi-component electrocatalysts to give enhanced catalytic performance and kinetics in the methanol electrooxidation thereby making a great impact in sustainable development goal to make clean energy research and technology more accessible including renewable energy and energy efficiency, as well as promoting investment(cost friendly) in infrastructure for energy and clean energy technologies.

1.2 RATIONALE AND MOTIVATION

Fuel cells have stimulated great attention as reliable power sources for mobile and portable electronic devices due to the depletion of fossil fuels and increasing environmental pollution. Among various types of fuel cells, direct alcohol fuel cells (DAFC) are excellent ones because of their low pollutant emission, high energy density *e.g.* 6.13kWh/g for DMFCs, low operating temperature, and the ease of handling a liquid fuel [4-7]. The direct methanol fuel cell (DMFC) which is a low-temperature fuel cell has attracted considerable attention for portable device applications and possesses several advantages. The use of liquid fuel is considered to be essential for commercial use because it can be easily transported and stored, less safety concern and a relatively small investment is needed for placing the relevant support infrastructure. Another advantage is that these fuel cells can achieve efficiencies of up to 40%. DMFCs are available on a limited scale; methanol fuel has an energy density that is higher than current petrol used and hydrogen. Additionally, methanol is a liquid, it can be easily integrated into existing fuelling infrastructure. DMFC systems are much more efficient than combustion engines, quieter, and less polluting. DMFCs are available at a very high cost because of the electrocatalyst used which is platinum-based and can be very expensive. This can be overcome by using reduced amounts of the catalyst without reducing the efficiency of the cell or non-platinum-based catalysts or binary/ternary alloy of the metal for by-functional or electronic effects. Hence, the focus of my research is to add Iridium, Molybdenum, and Tungsten to the PtRu electrocatalysts.

1.3 AIMS AND OBJECTIVES OF THE STUDY

This research aims to produce efficient ternary catalysts, PtRuIr/MWCNT, PtRuMo/MWCNT, and PtRuW/MWCNT as anode catalysts for methanol electrooxidation. This is to be achieved by identifying the best PtRu/MWCNT preparation method from four catalyst preparation methods, namely, impregnation method, polyol method, modified polyol method, and microwave-assisted modified polyol method and characterization of the resulting catalysts by electrochemical methods (including cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy), elemental analysis (by EDS), and physical characterization (by TEM and XRD).

Once the best preparation method had been established, ternary catalysts PtRuIr, PtRuMo, and PtRuW dispersed on multiwalled carbon nanotubes (MWCNT) will be developed and characterized physically and electrochemically as mentioned above and compared will the performance of the binary PtRu/MWCNT catalyst to come out with the ternary most suitable for DMFC system application. The binary PtRu/MWNT will also be heat treated for temperature optimization.

The objectives of the study are as follows:

1. To synthesize binary catalyst PtRu dispersed on multiwalled carbon nanotubes (MWCNT) using the impregnation method.
2. To synthesize binary catalyst PtRu dispersed on multiwalled carbon nanotubes (MWCNT) using the polyol method.
3. To synthesize binary catalyst PtRu dispersed on multiwalled carbon nanotubes (MWCNT) using the modified polyol method.
4. To synthesize binary catalyst PtRu dispersed on multiwalled carbon nanotubes (MWCNT) using the microwave-assisted modified polyol method.
5. Heat treatment of the binary PtRu/MWCNT synthesized by the best catalyst preparation method at 2500C, 3500C, and 4500C for optimization.
6. Developing ternary catalyst PtRuIr/MWCNT, PtRuMo/MWCNT, and PtRuW/MWCNT using the best catalyst preparation method, microwave-assisted modified polyol method.
7. To characterize the morphological, structural, and elemental composition properties of the synthesized catalysts by high-resolution transmission electron microscopy (HRTEM), X-ray Diffraction(XRD), and energy dispersive spectroscopy (EDS) respectively. Electrochemically, cyclic voltammetry will be used for the electroactive catalyst surface area and electroactivities of the synthesized catalysts towards methanol electrooxidation, Chronoamperometry and electrochemical impedance spectroscopy will be used for stability and kinetics of the catalysts towards methanol oxidation reaction.

1.4 THESIS OUTLINE

Chapter 1: Chapter one gives the introduction and background to the study, the rationale and motivation, research aims, and objectives.

Chapter 2: It presents a detailed review of fuel cells, choice of carbon nanotubes, anode Catalysts, catalyst preparation methods.

Chapter 3: Experimental. Outlines the methods employed when producing the catalysts and analytical techniques.

Chapter 4: Reports on the four catalyst preparation methods synthesis and characterization of the synthesized binary PtRu/MWCNT catalysts.

Chapter 5: Reports on the effect of power controlled microwave assisted modified polyol on the morphological, structural, and electrochemical properties of binary PtRu/MWCNT and ternary PtRuIr/MWNT, PtRuMo/MWCNT PtRuW/MWCNT catalysts synthesized.

Chapter 6: Reports on the effect of heat treatment on the morphological, structural, and electrochemical properties of binary PtRu/MWCNT synthesized.

Chapter 7: Conclusions and Recommendations for future research

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CHAPTER TWO

LITERATURE REVIEW

2.0 INTRODUCTION

Platinum or platinum-based materials are used in most fuel cell catalytic electrodes, including DMFC anodes [1]. Many issues that are preventing the commercialization of DMFCs, including low performance, catalyst instability, methanol crossover, and temperature and water control, are yet to be addressed [2–4]. Catalyst poisoning [5, 6] occurs when a pure platinum catalyst is used for methanol electrooxidation due to the adsorption of CO [7], one of the intermediates by blocking the reaction's active sites, resulting in slow reaction kinetics. As a result, the goal of this research is to develop ternary catalysts as anode catalysts for DMFC that provide the best methanol oxidation kinetics.

The best single-metal catalyst for this reaction has been discovered to be platinum. However, the creation of linearly deposited CO species poisons the electrode surface, limiting the oxidation reaction. The alloying of platinum with other metals, such as Ru, Sn, W, Mo, Os, and Ni, is a handy approach to changing the electrocatalytic characteristics of platinum to lessen or avoid the poisoning effect. The presence of a second alloying component can increase the activity of platinum-based catalysts through electronic effects or a bifunctional mechanism in which platinum dissociates methanol via chemisorption and the second metal activates water, resulting in oxygen-containing species forming at lower potentials, thereby facilitating the overall reactions on the catalysts. Many studies have been undertaken on the development of Pt-based binary catalysts, such as Pt–Ru [8–14], Pt–W [15, 16], Pt–Mo [17], Pt–Sn [17–19], and Pt–Os [20, 21], to improve catalytic performance and reduce the poisoning impact of anode catalysts. As a result of these studies, it has been determined that Pt–Ru complexes are particularly effective anode catalysts for methanol electro-oxidation due to the bifunctional mechanism and electronic effects [8, 9, 22].

More work is being done to develop new methanol oxidation catalysts based on PtRu ternary catalysts such as PtRuNi, PtRuMo, and metal oxides. In comparison to PtRu/C, researchers like ZB Wang et al. [23] and M Gotz et al. [17] reported on the methanol oxidation of several ternary PtRu-based catalysts like PtRuNi/C, PtRuSn, PtRuW, and PtRuMo. Using electrochemical techniques, they discovered that PtRuNi/C, PtRuW/C, and PtRuMo/C had higher electrocatalytic activity than PtRu/C, but other ternary PtRu, such as PtRuSn, had lower activity. The promoting impact of such metals is attributed to the bifunctional mechanism and electronic action of Mo metal, which explains their increased catalytic activity. In this study, the methanol electrooxidation on PtRuW/MWCNT, PtRuMo/MWCNT, and PtRuIr/MWCNT electrocatalysts prepared by power-controlled microwave-assisted modified polyol method is reported compared to ZB Wang et al. [23] and M Gotz et al. [17] that reported impregnation reduction method and both impregnation and colloid methods of catalyst preparation respectively. According to ZB Wang et al [23] sodium borohydride was used in the manufacture of the PtRuMo catalyst to chemically reduce the precursors H2PtCl6, RuCl3, and (NH4)6Mo7O24 in varied atomic ratios. PtRuMo in a molar ratio of 6:3:1 showed stronger catalytic activity and durability for the MOR than manufactured PtRu/C and Pt/C. In this study, H2PtCl6, RuCl3, and MoCl3 precursors were used. All the ternary catalysts PtRuW/MWCNT, PtRuMo/MWCNT, and PtRuIr/MWCNT were also synthesized in a molar ratio of 1:2:2. According to the bifunctional effect, Mo combined with Ru promotes H2O activation more than Ru alone, which then promotes CO oxidation, resulting in increased MOR activity. Lamy et al. [24] produced a chart of several PtRu-based ternary catalysts.

2.1 FUEL CELL

A fuel cell is a type of device that generates electricity through chemical reactions. The cell can continue to produce electricity as long as fuel is available [25, 26]. Fuel cells are compatible with other renewable and modern energy sources, such as wind energy, solar energy, and hydroelectricity, all of which are dedicated to the production of sustainable electricity. Some of the features associated with these devices include their silent operation without vibration, inherent modularity that allows for simple construction, and a wide range of applications in portable devices, stationary units, and transportation [27].

They offer a cleaner and more flexible chemical-to-electrical energy conversion than fossil fuel combustion. In this regard, it is important to note that the combustion of fossil fuels has increased air pollution and greenhouse gas emissions such as CO2, resulting in climate change, ozone depletion, and acid rain [26, 28]. For these reasons, since the Kyoto Protocol also suggested the use of renewable energy sources, the promotion of existing high-efficiency electricity technologies, and the adoption of advanced low-CO2 emission energy systems, there has been intensive research and development of renewable and environmentally friendly ways to generate electricity [26, 29].

Fuel cells are essentially electrochemical devices that transform chemical energy directly into electricity, with water and heat as by-products [27]. The device is composed of four major components: anode and cathode electrodes, an electrolyte, and a gas diffusion layer. The anode electrode in the device is fed with fuel, while the cathode electrode is fed with oxygen or air. The major objective of an electrolyte, which is located between the electrodes, is always to transport ions (anions or cations) from one side to the other, regardless of the kind of cell [30] Sir William Grove presented the first fuel cell in the early 1800s when he built a device that combined hydrogen and oxygen to produce electricity, which he termed the gas battery. This device was later referred to as a fuel cell. Francis Thomas Bacon demonstrated the first fully operational fuel cell in 1959 [27, 28]. There are various types of fuel cells available today, each with its own chemical fuel feed and operating principles.

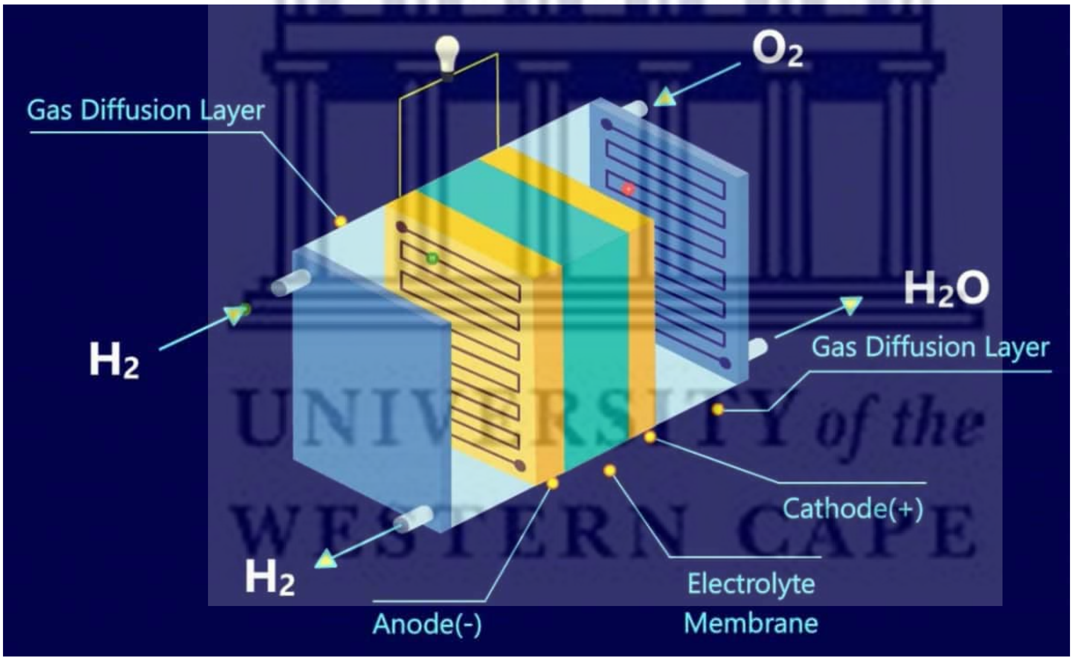

Figure 2. 1: Schematic diagram of a hydrogen fuel cell [31]

Analogous cathode and anode reactions for a H_2 fuel cell are:

Cathode: $1/2O_2+2H^++2e^-\rightarrow H_2O$

Anode: $H_2\rightarrow 2H^++2e^-$

Overall reaction: $1/2O_2+H_2\rightarrow H_2O$

2.2 TYPES OF FUEL CELLS

The type of electrolyte used in fuel cells is the most important distinction. This classification affects the type of electrochemical processes that occur in the cell, the type of catalysts required, the operating temperature range, the fuel required, and other criteria. [32]. These properties have an impact on the applications that these cells are best suited for. There are varieties of fuel cells in research right now, each with its own set of benefits, drawbacks, and prospective applications [32]. Proton electron membrane fuel cell, PEMFC, direct methanol fuel cell, alkaline fuel cell, phosphoric acid fuel cell, solid oxide fuel cell, and molten carbonate fuel cell are the different types of fuel cells.

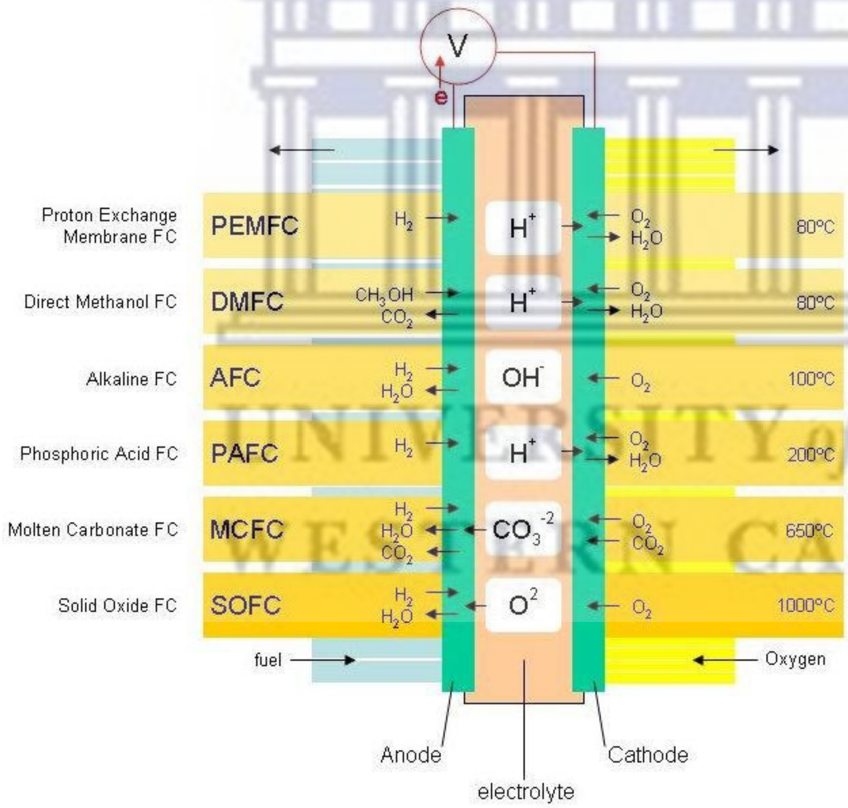

Figure 2. 2**:** Schematic diagram of different types of fuel cells, and their operating temperatures [29]

2.2.1 PROTON EXCHANGE MEMBRANE FUEL CELL

The electrolyte in PEMFC is a polymeric membrane, which transports protons produced by the hydrogen oxidation reaction at the anode to the cathode, where they participate in the oxygen reduction reaction. Meanwhile, the only by-products are water and heat. One of the benefits of PEMFC is that it reduces wear on system components, which improves cell durability. This is due to the low operating temperature, which allows for quick start-up (low warm-up time). This, combined with the cell's extremely high-power density, makes them excellent and competitive for commercial portable devices such as laptops, computers, and mobile phones, as well as transportation and stationary power. The membrane electrode assembly (MEA) is the heart of PEMFCs, where the electrochemical reactions take place to generate electrical power. The MEA consists of a proton exchange membrane, catalyst layers (CLs), and gas diffusion layers (GDLs). Typically, these components are manufactured separately and then pressed together at high temperatures and pressures. An ideal MEA would make all active catalyst sites in the CL accessible to the reactant (H_2 or O_2), protons, and electrons, facilitating the effective removal of generated water from the CL and GDL.

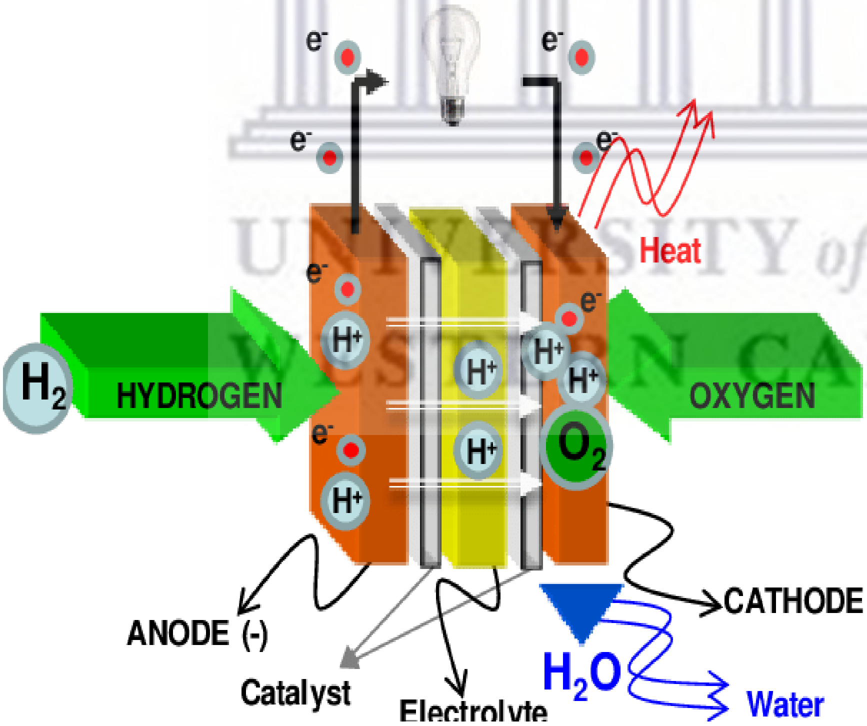

Figure 2. 3: Schematic diagram of a PEMFC fuel cell [33]

2.2.2 ALKALINE FUEL CELL

AFCs are classified into three types: mobile electrolyte, static electrolyte, and dissolved fuel. In the space program, both mobile and static electrolytes are utilized. As a fuel, an alkaline solution (OH^- ion flowing across the electrolyte) is used in this fuel cell. When compared to the Proton exchange membrane fuel cell, this fuel cell offers various advantages, including a low activation overpotential at the cathode, a high working voltage, the use of non-precious metals, the absence of bipolar plates, and fewer water management issues (PEMFC). The main disadvantages of AFCs are their low power density and the fact that CO_2 is toxic to the fuel cell. The space program was the first genuine application of fuel cells. The movable electrolyte system was first utilized in AFCs in the 1940s and is now used in terrestrial systems. A static electrolyte system is used by the shuttle orbiter [34].

Anode reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ (2.1)

Cathode reaction: $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (2.2)

Overall reaction: $H_2 + 1/2O_2 \rightarrow H_2O$ (2.3)

2.2.3 MOLTEN CRABONATE FUEL CELL

Molten sodium or magnesium carbonates are used as electrolytes in molten carbonate fuel cells. When running at 650 °C, efficiency ranges from 60 to 80%. Some studies reported up to 2 MW single-stack performance and up to 100 MW multi-stack performance [35]. It is possible to limit the damage caused by carbon monoxide and recycle the heat produced during operation in these cells. The use of nickel electrocatalysts, as opposed to platinum electrodes utilized in other fuel cells, accounts for the low cost of these devices. High operating temperatures, on the other hand, limit the safety of MCFCs and necessitate the use of corrosion-resistant materials [35].

Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ (2.4)

Cathode: $1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ (2.5)

Overall reaction: : $H_2 + 1/2O_2 \rightarrow H_2O$

2.2.4 PHOSPORIC ACID FUEL CELL

PAFC employs liquid phosphoric acid as an electrolyte. Due to the weak conductivity of the electrolyte, the cell functions at temperatures ranging from 100 to 250 °C. However, because PAFC employs hydrogen as a fuel and does not require the usage of pure hydrogen due to high operating temperatures, and because the electrolyte does not react with CO_2 to generate carbonate ions, this is also a benefit. PAFCs can tolerate carbon monoxide poisoning if the concentration of the gas is less than 1.5%, and carbonate production is not a hazard for PAFCs. The only significant disadvantage is the employment of an expensive platinum catalyst [36].

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (2.6)

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (2.7)

Overall reaction: $H_2 + 1/2O_2 \rightarrow H_2O$ (2.8)

2.2.5 SOLID OXIDE FUELL CELL

Electrolytes in solid oxide fuel cells are ceramic calcium or zirconium compounds. With working temperatures of up to 1000 °C and outputs close to 100 kW, efficiencies are close to 60%. A reformer is not required to extract hydrogen from the fuel at these high temperatures, but this factor also prevents the use of SOFCs in other electrical devices [37].

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (2.9)

Cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ (2.10)

2.2.6 DIRECT METHANOL FUEL CELL

The majority of fuel cells run on hydrogen, which can be delivered directly into the system or created within the system by reforming hydrogen-rich fuels like methanol, ethanol, and hydrocarbon fuels. Direct methanol fuel cells (DMFCs), on the other hand, run on pure methanol, which is combined with water and delivered directly to the anode of the fuel cell.

Because methanol has a higher energy density than hydrogen—though not as high as gasoline or diesel fuel—direct methanol fuel cells avoid many of the fuel storage issues that plague other fuel cell designs. Because methanol is a liquid, like gasoline, it is also easier to transport and deliver to the general population utilizing existing infrastructure. DMFCs are frequently used to power portable devices like cell phones and laptop computers [38].

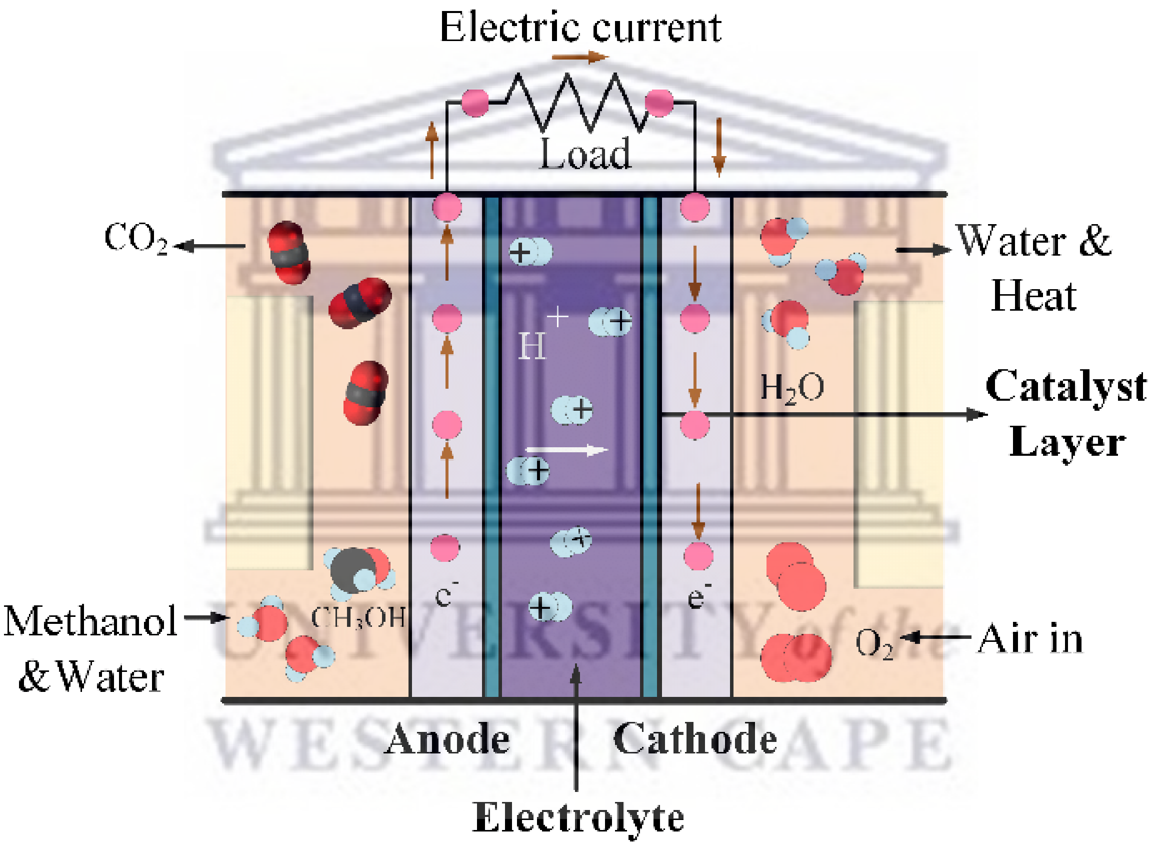

Figure 2. 4**:** Schematic representation of Direct Methanol fuel cell, DMFC [38]

In a DMFC, methanol is electrochemically oxidized at the anode electrocatalyst to produce electrons that travel through the external circuit to the cathode electrocatalyst where they are consumed together with oxygen in a reduction reaction. The circuit is maintained within the cell by conduction of protons in the electrolytes. Figure 2. 5 is a schematic illustration of the DMFC system that demonstrates the DMFC working principle. By oxidizing methanol to CO_2 and H_2O, the DMFC turns chemical energy into electrical energy. A proton-conducting solid membrane is sandwiched between porous structures and serves as both an electrolyte and ` separator between anode and cathode (such as nafion). The nafion acts as both current collectors and catalytic particle supports. [39]

A methanol molecule combines with an H_2O molecule at the anode, releasing CO_2, six protons that can migrate through the electrolyte to the cathode, and six electrons that can flow through the external load. Protons passing through the electrolyte and electrons passing through the externally loaded circuit must arrive at a catalyst nanoparticle on the cathode, where O_2 is electrocatalytically reduced and H_2O is generated. The following are the relevant electrochemical processes at the electrode surface in acidic media. [38]

Anode reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (2.11)

Cathode reaction: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (2.12)

Overall reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$ (2.13)

2.3 CATALYTS

A catalyst helps to speed up a chemical reaction by creating bonds with the molecules involved. The catalyst permits the reactants to react to produce a product, which then detaches from the catalyst and leaves it undamaged for the next reaction. As a result, a catalytic reaction may be thought of as a cyclic event in which the catalyst precipitates and then returns to its original state after the cycle.

Catalysts are the workhorses of chemical transformations in industry, accounting for 85-90 percent of total chemical output. A catalyst provides an alternative, more energy-efficient mechanism to the non-catalytic reaction, allowing activities to be carried out at pressures and temperatures that are industrially practical.

2.3.1 FUEL CELL ELECTROCATALYSTS

Catalysts are used in the anode and cathode regions of a fuel cell to speed up reaction kinetics. Efficient electrocatalysts are needed in fuel cells to increase cell's performance, notably its durability, stability, and activity, as well as to lower cost. PtRu catalysts are used due to its high CO tolerance through bifunctional mechanism. Because the catalysts used in fuel cells are noble metals and non-noble immobilized on a conducting support, the catalysts utilized in fuel cells are classed as heterogeneous. The reactants and the heterogeneous catalyst are in distinct phases.

2.3.2 ANODE CATALYSTS USED IN METHANOL OXIDATION

Noble metals (such as Pt, Pd, and Au) can considerably contribute to DMFCs as common catalysts for methanol oxidation [40-42]. As a result, a wide range of noble metal catalysts have been tested in DMFCs [40-42]. Cost reductions and increased methanol oxidation activity are especially promising. Noble metal catalysts' methanol oxidation activity is greatly influenced by particle shape, size, and surface structure [41]. As a result, numerous researchers have recently produced noble metal catalysts with varying sizes, shapes, and surface structures to boost methanol oxidation activity while decreasing metal loading [41-42]. For the past three decades, methanol oxidation has been widely researched. Only platinum and platinum-based catalysts have been found to be reactive and stable in the acidic environment of the DMFC [43, 44].

Another major problem for the efficient conversion of methanol fuel to electric current in a DMFC is the anode catalyst's sluggish MOR kinetics. This slowness is mostly due to surface poisoning by chemical intermediates such as COads-like species produced during the stepwise dehydrogenation of methanol [45-47].

As a result, MOR on Pt is only achievable at potentials when adsorbed COads-like species and other poisoning intermediates are successfully oxidized, resulting in considerable overpotential and DMFC efficiency loss [50]. PtRu [49, 50], PtSn [51, 52], PdNi [53], PtMo [54, 55], PtTiO2 [56, 57], PtW [54], PtOs [58], and PtMn [59] are examples of binary Pt-based alloy (double-component) catalysts. These alloyed metals can supply OH species at higher negative electrode potentials to react with COads-like poisoning species, hence enhancing methanol electrooxidation activities. Methanol oxidation and related mechanisms have been studied in various catalytic systems under well-defined circumstances [60, 61, 62, 63-68].

Platinum's electroactivity appears to be influenced by its morphology [69], with roughened platinum having significantly higher activity [70]. .

Several researchers have looked into the effect of particle size on methanol oxidation [74–76]. For particles with a diameter of less than 5 nm, several scientists have found a decline in activity as the particle size decreases [74-77].

On a pristine platinum electrode, linearly bound CO can cover up to 90% of the active sites, blocking the majority of them. These findings have been frequently confirmed by various researchers [78, 79, 80].

Platinum has been looked at a lot as an electrocatalyst for the oxidation of methanol. To remain being active it is used as a composite to avoid formation of CO. This has led to the search for other active materials, especially those that could work with platinum as a promoter by making it easier for chemisorbed CO to be oxidized [44].

Surface ad-atoms placed on the platinum surface, such as Au [81], Sn [84-88], Ru [86-88], Pb [86, 89], and Bi [84, 86, 90], can be used to promote platinum. Pt promotion can also be achieved by alloying platinum with other metals, with the second metal forming a surface oxide in the methanol oxidation potential region [44, 91]. Pt-Sn [82, 86, 92-94], Pt-Os and Pt-Ir [95], Pt-Pd [96], and Pt-Ru [83, 93, 95, 97-102] are examples of such alloys. WO_3 has also been studied as a Pt promoter [103-105]. Electrodeposited Mo on Pt has also been observed [106]. Hamnett et al. [103] reported the use of Pt as a promoter in the presence of a base-metal oxide (e.g., Nb, Zr, and Ta).

The Pt-Ru alloy has the highest methanol electro-oxidation activity of the binary Pt-based alloys [107]. According to studies on Pt-Ru, the reaction is triggered by the dissociative adsorption of methanol on platinum sites, resulting in the formation of a highly adsorbed intermediate, CO. At higher levels of polarization, water sticks to Ru sites and breaks apart. This makes a hydroxylic species, which then oxidizes CO. Water dissociates at lower potentials on Ru than it does on Pt, resulting in increased activity for Pt-Ru over pure Pt [108-110].

Ru has been found to improve anti-poisoning performance. However, the expensive cost of the Pt-Ru catalyst is one of the major barriers to its widespread application [111]. The extensive commercialization of DMFCs is mostly dependent on lowering the cost of the catalysts [112]. The difficulties mentioned above can be addressed by modifying Pt catalysts with other metals or metal oxides that have a stronger tendency to generate surface-oxygenated species at lower potentials. Several groups have made serious efforts to develop new catalyst systems for methanol oxidation based on multiple-component catalysts such as PtRuNi [113-115], Pt-Ru-Os [116], Pt-Ru-Mo-W [117] and Pt-Ru-Sn-W [118] The Pt-Ru-Sn system was also investigated [119], but it was discovered that alloying Pt-Ru with tin causes the Ru to be expelled, resulting in little benefit [120].

2.3.3 CATHODE CATALYSTS USED IN DMFC

The cathode electrode of DMFCs, like the anode electrode, lacks a suitable electrocatalyst. As a result, novel cathode electrocatalysts (cheap cost and longer durability) with strong electrocatalytic activity for the oxygen reduction reaction at low temperatures are required Noble metals contribute considerably to DMFCs as a common catalyst for the ORR [121-122]. However, some limitations, such as slow kinetics and poor electrocatalyst durability of the ORR at the cathode, continue to limit the efficiency of DMFCs. As a result, the creation of a highly active and long-lasting catalyst is widely desired in order to increase the ORR performance of DMFCs.

Materials scientists have reported many single-component catalysts over the past decade. Several single-component catalysts have been developed, including Ag [122], Au [122,123], Pt [123], and Pd [124,125] that have exhibited an increase in ORR activity. Among these catalysts, nanostructured Pt has consistently been a great electrocatalyst for ORR but is extremely costly for commercialization in DMFCs. [126]

Double-component nanostructures are being developed to make use of Pt loading in a limited resource. Wang et al. [127] reported that combining a metal X (such as Co, Ni, Cr, or V) with limited occupancy of d-orbitals with another metal X' (such as Pd, Ag, and Au) with fully occupied d-orbitals would increase ORR activity [128]. The d-orbital coupling effect between metals can significantly reduce the Gibbs free energy for the ORR electron transfer steps, resulting in improved ORR kinetics.

2.4 ACTIVITY AND REALIABILITY OF ANODE ELECTROCATALYSTS USED IN DIRECT METHANOL FUEL CELL

Some technical challenges are still hindering the commercialization of DMFC, two major ones are slow methanol oxidation kinetics even on some state-of-the-art anode catalysts and methanol crossover through the membrane thereby depressing cathode performance and reducing fuel efficiency. Researchers have focused on these two areas in recent times namely exploring new anode catalysts that can effectively improve the methanol electro-oxidation kinetics and seeking novel cathode catalysts that will tolerate methanol crossover. With the keen interest of reducing cathode performance depression induced by methanol crossover, some activities on methanol-tolerant cathode catalysts have also been carried out [129]. Platinum/ruthenium alloys are the most practical anodic electro-catalysts used as anode catalysts for the DMFC application for they exhibit reasonable activities and stability. For a single noble metal platinum electrocatalyst the adsorption of CO, one of the intermediates in methanol electro-oxidation, can inhibit the reaction active sites, resulting in slow reaction kinetics. Using a second metal, such as ruthenium, alloying with platinum the oxidation kinetics of methanol are increased significantly reaching a practicable level. The mechanism of methanol oxidation on the Platinum surface has been investigated extensively for decades.

As reviewed by Lamy et al. [130] and Arico et al. [131], many works have been devoted to the optimization of Pt–Ru catalytic performance towards methanol oxidation. The current consensus is that the optimal Pt/Ru ratio is 1:1, and the particle sizes are better brought down to the nanoscale in order to improve catalyst utilization. However, in order to achieve acceptable fuel cell performance from the practical point of view in a real fuel cell environment, a high catalyst loading of about 2–8 mg cm^{-2} is required, even when using a 1:1 Pt–Ru alloy catalyst, especially when considering the durability of the fuel cell. This high noble catalyst loading leads to high cost, hindering the commercialization of DMFCs. Therefore, alloying other metals to platinum to develop a binary or ternary component for further improvement of activity and optimization of catalyst utilization is key.

2.5 NARROWING THE FIELD OF CHOICES OF ANODE HYBRID CATALYSTS

Exploration of new catalysts in a fast way is one of the major objectives in DMFC Research and development. For several decades many studies have been involved in exploring platinum based ternary and quaternary alloys, other noble metals and non-noble metal alloys and compounds as alternatives to the Pt–Ru anode catalyst, and some great achievement has been made. For example, molybdenum oxides and tungsten were demonstrated to be good surface promoters for improving Pt activity towards methanol oxidation due to their special "spillover" effect [131]. However, conventional methodologies of catalysts exploration are labour-intensive, time-consuming and inefficient. A rapid and efficient screening approach is urgently needed to speed up the discovery of new DMFC anode catalysts and catalyst activity optimization.

Whitacre et al. reported some preparation methods [132]. A combinatorial co-sputtering approach to screen fuel cell catalysts for methanol oxidation was done. Sputter deposition was used to batch fabricate multiple thin-film samples on a micro-fabricated Au multielectrode, which served as the current collector, at room temperature. This combinatorial technique was applied to examine a binary Pt–Ru system and a quaternary Ni–Zr–Pt–Ru system. Jayaraman et al. [133] reported an automated combinatorial screening system using pulsed potential electrodeposition to prepare catalyst arrays. This system was used to synthesize and screen Pt–WO_3 catalysts for methanol oxidation. XPS measurements showed that the electrodeposited film is amorphous and not alloyed between Pt and W. The electrodeposition method has some limitations, especially in controlling the composition due to the different metal deposition rates. According to Reddington et al. [134] a combinatorial method by using a fluorescence acid–base indicator to optically screen electrochemical catalysts for methanol oxidation. They developed quaternary and five-pick-four arrays containing Pt, Ru, Ir, Os or Rh by inkjet printing followed by borohydride reduction. The activities of multi-component catalysts towards methanol oxidation were identified by the indicator's fluorescence images, which respond to proton concentrations. Applying this combinatorial analysis, $Pt_{44}Ru_{41}Os_{10}Ir_5$ was discovered to be the best quaternary formulation. Comparing the performance of a $Pt_{44}Ru_{41}Os_{10}Ir_5$ catalyst prepared by borohydride reduction with a commercially available Pt–Ru catalyst showed that the former was significantly more active than the latter in DMFC testing at 60^0C. Choi et al. [135] also used a similar optical screening method to investigate quaternary catalysts containing W and Mo for methanol oxidation. It was discovered that a quaternary catalyst with a formulation of $Pt_{77}Ru_{17}Mo_4W_2$ showed much better electrochemical activity and stability than $Pt_{50}Ru_{50}$ formulation.

2.6 CARBON SUPPORTS

The stability of a supported catalyst is much better than that of an unsupported catalyst when it comes to the number of catalytic sites that build up when the fuel cell is working. Carbon supports are commonly utilized in fuel cells The high electronic conductivity of the carbon support makes it possible for electrons to move from the catalytic sites to the conductive carbon electrodes and then to the outside circuit.

Carbon black is created when any carbon-containing material is burned in an inert, oxygen-free atmosphere. Carbon black was formerly thought to be an amorphous type of carbon with nearly spherical graphite particles [136]. Particles with a diameter of less than 50 nanometers may cleave to form particle aggregates and agglomerates with a diameter of roughly 250 nanometers. The particles exhibit para-crystallite structures, which are non-discrete 3D groups formed by an assembly of parallel layers [136]. Carbon black's shape and particle size distribution are determined by the source material and the thermal decomposition process. Particle size and distribution, which are the most important properties of carbon black for end-use applications [137, 138], also play a role in figuring out the safe area.

2.7 THE CHOICE OF NANOSTRUCTURED CARBON SUPPORTS

A series of new nanostructured carbon materials were explored as catalyst supports in recent decades. The family of carbon nanotubes (CNTs) is the most well-known nanostructured carbon, which has shown very promising results in catalyst support for fuel cell applications due to their unique structural and electrical properties. The reported studies have shown that CNTs were superior to carbon blacks as catalyst supports for proton exchange membrane fuel cells (PEMFCs) [138,139]. A Multi- walled carbon nanotubes supported Pt catalyst with 12 wt.% Pt loading could give a 10% higher fuel cell voltage, and twice the power density than that of carbon black supported with 29 wt.% Pt loading [140,141]. On the other hand, in recent years, many studies have explored CNTs as supports for DMFC catalysts. Che et al. [138] reported that the current density of methanol oxidation on a Pt/MWCNT catalyzed membrane electrode was 20 times higher than that of a bulk Pt electrode. Li et al. [143–145] reported that multi-wall carbon nanotube (MWNT) supported catalysts showed better performance in DMFCs compared to those supported by carbon black (XC-72) under identical conditions both in half-cell characterization and in a fuel cell performance test. Their results showed that the mass activity of Pt/MWNT catalyst at 0.7V (versus DHE) in a single cell testing was 14.7mAmg−1 (Pt), much better than Pt/XC-72 catalyst (2.2mAmg−1 (Pt)).

Rajesh et al. [146,147] studied methanol oxidation reactions catalyzed by various metal catalysts supported on CNTs and commercially available Vulcan carbon. The activity and stability of these electrodes were ranked from highest to lowest as Pt–WO_3/CNT > Pt–Ru/Vulcan > Pt/CNT > Pt/Vulcan > bulk Pt. Single-wall carbon nanotube (SWNT) supported Pt electrodes were also reported to show higher catalytic activity both for methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) than that seen in an unsupported Pt electrode [148]. The authors studied the kinetics of a methanol oxidation reaction (MOR) on a Pt/SWCNT electrode and found that the onset potential of methanol oxidation on this electrode was ~200mV versus SCE which was 200mV lower than that of the unsupported Pt electrode (400mV versus SCE). The higher catalytic activity was thereby attributed to the larger surface area of carbon nanotube architecture and the lower overpotential for methanol oxidation. Therefore, CNTs appear to have promising potential as catalyst supports for DMFCs.

Despite these findings, the CNT synthesis, metal loading and electrode preparation based on CNT supports still face some challenges, especially when applied to fuel cells. CNTs are usually synthesized by carbon-arc discharge, chemical vapor deposition (typically on catalytic particles), or laser ablation of carbon. These synthetic methods have their limitations in terms of large-scale production and cost-effectiveness. Their harsh preparation conditions and low yield products are major disadvantages. Currently, SWCNTs are produced only on a very small scale and the process is extremely costly [149]. The key thing is to further develop industrial large-scale production of CNTs to meet the needs of all the possible applications, including the fuel cell industry. High dispersion metal nanoparticle loading onto CNTs is not an easy task. Several methods have been developed to prepare highly dispersed metal/CNT catalysts. The conventional impregnation method was frequently used to deposit metal nanoparticles onto CNTs [142]. Using this method, Che et al. [142] deposited Pt–Ru alloy particles with a very narrow particle size distribution onto the CNT. However, conventional impregnation techniques based on wet impregnation and chemical reduction of the metal precursors are time consuming and the produced catalysts are easily contaminated by some side-products. Alternatively, the electrodeposition method was used to make CNT supported catalysts because of its high purity and simplicity [150]. However, due to the concurrent reduction of protons, it is difficult to estimate the loading of the metallic catalyst. It was also difficult to attain small nanoparticles by the electrodeposition method.

P. Serp et al [151] and H.I. Han et al [152] found that the surface modification of CNTs before the metal deposition was important for achieving optimal interaction between the support and the catalyst precursor. Due to the pristine surface of CNTs which is inert, it is difficult to attach metal nanoparticles to the substrate surface. Through surface functionalization or modification or pre-treatments, some anchoring sites were introduced to the surface so the metal nanoparticles could easily attach onto the CNTs` surface. Recently, the most widely used pre-treatment is refluxing CNTs in nitric acid to create an acid site on the surface, which can act as a nucleation center for metal ions [153].

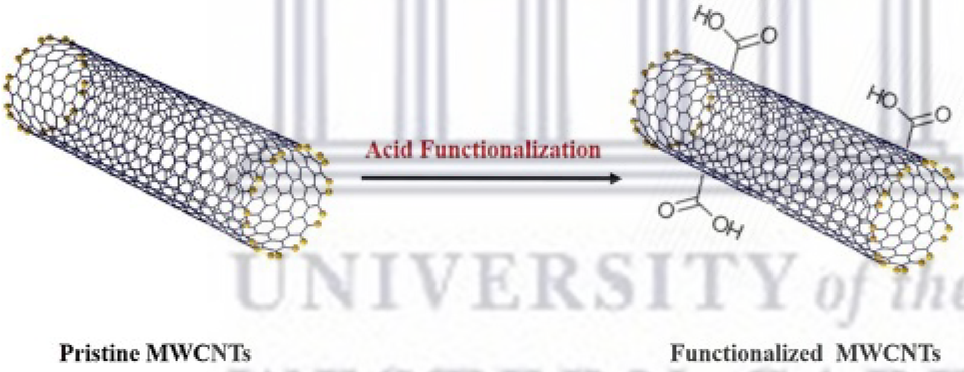

Figure 2. 5**:** Schematic diagram of functionalization of Multiwalled carbon nanotubes and applications. [154]

2.8 ELECTROCATALYSTS PREPARATION METHODS

One of the key areas in DMFC anode catalyst research is the development of Pt–Ru catalysts. To achieve great dispersion and maximum utilization while preventing catalyst agglomeration during fuel cell operation, the bimetallic Pt–Ru catalyst has been supported on several high-surface-area materials, such as carbon particles. Even though unsupported Pt–Ru catalysts have received some attention in recent years [155–157], the most recent papers have mostly focused on supported Pt–Ru/C catalysts. The essential criteria for a high-performance catalyst are (1) a consistent composition throughout the nanoparticles; (2) a narrow nanoscale particle size distribution; (3) a fully alloyed degree; and (4) good dispersion on a carbon support. Some new and cost-effective preparation methods have been developed based on these criteria, and they appear to be promising for achieving performance optimization by managing synthetic procedures and circumstances.

Pt-Ru catalyst can be made using a variety of chemical processes. The reduction of metal chloride salts is a typical procedure, but this preparation process results in high levels of chloride poisoning. The most popular method for chemical preparation involves first oxidizing, then reducing, metal sulphite salts, which can be made from metal salts with chlorides [160, 159]. The Bönnemann group [160, 161] and later other groups [162, 163] synthesized colloidal precursors for carbon-supported and unsupported Pt-Ru catalysts using the Bönnemann approach. A Pt-Ru catalyst that had been changed by metal oxide was also created [148]. Dickinson et al. [163] also suggested a different approach, in which the catalyst is made from carbonyl metal complexes by depositing the precursors on carbon in a solvent with a high boiling point.

The polyol process falls under the colloidal methods category when it comes to the manufacture of catalysts. By decreasing their ionic salts, the polyol process is a common method for creating bimetallic metallic nanoparticles in solution [165]. The polyol process involves suspending a powdered inorganic metallic compound in a liquid polyol (ethylene glycol). The suspension is heated to a specific temperature while being agitated. Within a few hours, the compounds can be completely reduced, and the recovered metal is a fine powder [165]. The process may also be carried out at room temperature, and since no additional heat is needed, the reaction requires less energy, which is advantageous for scaling it up. The reaction typically uses sodium borohydride as a reducing agent when it is conducted at room temperature [167].

In other instances, the polyol technique has been altered to produce even smaller particles and better dispersion. The problem with the polyol method is that it is hard to choose the right hydroxyl for each process.

But the low operating temperatures of the polyol technique, which allow the process to regulate particle characteristics like size, shape, and homogeneity, are a big advantage. In contrast to the impregnation method and the sulphite complex route, which both have chlorine impurities, the polyol method makes organic-free powders that are very pure.

L. Khotseng et al [168] reported a modified polyol method of catalyst preparation where a 10 μm of MWCNTs was soaked in a mixture of nitric and sulfuric acids and then refluxed for 5 h under refluxing conditions at 120°C with a constant flow of nitrogen gas to remove impurities on their outer walls and to introduce on the surface of the MWCNT functional groups known to be essential in enhancing catalyst loading and dispersion of the catalyst on the support. The MWCNTs were then rinsed with ultra-pure water until pH neutral was obtained before being oven-dried overnight at 100 °C. The materials employed were molybdenum (IV) oxide (MoO_2) and titanium (IV) oxide (TiO2), also known as anatase. The polyol reduction process was used to make supported 20 wt percent PtRu (1:1 a/o) and 20 wt percent PtSn (3:1 a/o) electrocatalysts [170]. Because of its inherent advantages, such as homogenous distribution and tiny particle size [153, 170], ethylene glycol (EG) was chosen as the reducing agent and stabilizer [153]. Jeng et al. [170] provided the process for making catalysts. The binary catalysts were created using 75 mg of MWCNTs impregnated with 60 ml of EG. To make a homogeneous paste, the mixture was sonicated for 15 minutes and then stirred for another 30 minutes. In a separate beaker, 40 mg of H2PtCl6H2O and 2 milligrams of $RuCl_3$ were dissolved in 10 ml of EG as Pt and Ru electrocatalyst precursor salts, respectively. After that, the salt/EG solution was added to the MWCNT/EG paste, and the pH was adjusted to roughly 2–4 by dropping in appropriate volumes of 4 M NaOH drop by drop. For the metal salts to cling to the surface of MWCNTs, the mixture was subjected to high-speed stirring for an hour. The mixture was then refluxed for 3 hours at 150°C under continuous nitrogen flow, then allowed to cool before being rinsed with ultra-pure water. Finally, it was dried overnight in the oven at 60°C. The same procedure was followed to deposit 20% PtSn/MWCNTs, with the exception that the pH was adjusted to around 13–14. The precursor salt utilized was $SnCl_2H_2O$. They used the same method for putting down 20% PtRu and 20% PtSn electrocatalyst on MoO_2 and TiO_2.

In a one-pot wet chemical reduction procedure, Narayanamoorthy B. et al. [172] used the following synthesis strategy to produce 20 percent Pt-Ir supported over MWCNT. In 45 ml of UHP water, 2 ml of 0.005 M $IrCl_3$ and 3 ml of 0.05 M sodium citrate dihydrate were added and agitated thoroughly for 15 minutes. Drop by drop, 5 ml of freshly prepared 0.1 M $NaBH_4$ was added to this mixture, followed by 0.5 ml of 30% H_2O_2 in an inert (argon gas) environment for 120 minutes. Then Pt was added by adding 1.53 ml (0.02 M) of an aqueous solution of $H_2PtCl_6.6H_2O$ and then 3 ml of formic acid. The temperature of the reaction was then raised to 160^0C for 60 minutes in an inert (argon gas) environment with constant stirring. Finally, the Pt-Ir alloy nanoparticles were decorated on conductive carbon support by distributing 31 mg of acid-treated MWCNT into the reaction mixture and letting it sit for 120 minutes under the same reaction conditions. The atomic ratio between Pt and Ir in this technique was changed to 3:1, 2:1, and 1:1 based on elemental composition and weight percent on MWCNT. Pt over MWCNT (20% Pt/ MWCNT) was produced under comparable conditions without the use of Ir precursor or $NaBH_4$ for comparison.

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CHAPTER THREE

3.1 MATERIALS AND REAGENTS

The chemicals utilized in the preparation were 0.61M of $H_2PtCl_6.6H_2O$ (5g of Chloroplatinic acid in 20ml of water), $RuCl_3$ (98%), $IrCl_3$ (99%), $MoCl_3$ (99.9%) and WCl_4 (99%) purchased from SA Precious Metal PTY Ltd. $HClO_4$(70%), HCl (32%) and $NaBH_4$(99.9%) were purchased from Sigma Aldrich Chemical Co., sodium hydroxide NaOH (Alfa Aesar) and ethylene glycol (99.9%), methanol (99.9%), HNO_3 (60%), and H_2SO_4(99.9%), purchased from Kimix Chemical and Lab supplies, cc, Cape Town, WC, South Africa, isopropanol C_3H_8O (99.5%) (Alfa Aesar) while Nafion solution (5 wt % solution) was purchased from Ion Power Inc. All the chemicals were utilized as received with no additional treatment. The multi-walled carbon nanotubes (MWCNTs) were bought from Carbon nano-material Technology Co. Ltd., Gargdong Gyongju, Gyeonggi, South Korea, with a width of ~20 nm and a length of ~10 µm. Before the MWCNTs were used, they were first functionalised in a hot solution consisting of a mixture of HNO_3 and H_2SO_4 (Kimix Chemical and Lab supplies, cc., Cape Town, WC, South Africa) (3:1) v/v. [156]. All synthesis was done using deionized water from the Milli-Q water purification system (Millipore, Bedford, MA, USA).

3.2 SYNTHESIS AND EXPERIMENTAL PROCEDURE

3.2.1 FUNCTIONALIZATION OF MWCNTS

1. 2g of MWCNTs was added to (3:1 ratio) HNO_3/H_2SO_4 mixture, made up of 90 ml HNO_3 and 10 ml H_2SO_4, the mixture was refluxed for 6 hours at 60ºC.
2. The carbon nanotube sediments were separated from the reaction mixture, and washed with ultrapure water. The synthesis solution pH was adjusted to ∼7 by washing with ultrapure water.
3. The purified, acid-functionalized MWCNT slurry was then oven-dried at 60º C overnight to obtain the black nanoparticles.

3.2.2 PREPARATION OF BINARY CATALYST PtRu/MWCNT

The PtRu bimetallic nanoparticle catalysts were supported onto the walls of MWCNTs by first using the four catalyst preparation methods, impregnation, polyol,modified polyol and microwave-assisted modified polyol reduction methods.

3.2.2.1 MODIFIED POLYOL METHOD

Catalysts were prepared by following the procedures of Jeng et al. [16] and L. Khotseng et al [18] methods of Platinum-based binary catalyst synthesis with little modifications. Ethylene glycol (EG) which acts both as the reducing agent and stabilizer [6] was chosen because of its inherent advantages which include the homogeneous distribution and small particle size [6, 27]

1. 75mg of MWCNTs were added to 60ml ethylene glycol (EG) for the ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRu (1:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6 \cdot 6H_2O$ and 0.1544mmol of $RuCl_3$ used as Pt and Ru precursor salts respectively, were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH was adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs. After that, the mixture was refluxed for 3 h at 160 °C under a continuous flow of nitrogen; it was then left to cool down and then washed with ultra-pure water.

5. Finally, the mixture was then filtrated and the residue (PtRu/MWCNT nanoparticle) was oven-dried at 60 °C overnight and PtRu/MWCNT catalyst will be obtained

3.2.2.2 POLYOL REDUCTION METHOD

The same procedure was followed for the Polyol method using $NaBH_4$ as a reducing agent and ethylene glycol as the stabilizer as follows

1. Then 75mg of MWCNTs was added to 60ml ethylene glycol (EG) for the ratio of (1:1), the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRu (1:2 atomic ratio) was prepared with a calculated amount of 0.0772 mmol of $H_2PtCl_6 \cdot 6H_2O$ and 0.1544mmol of $RuCl_3$ used as Pt and Ru precursor salts respectively, were added and dissolved in a 3:1 of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH was adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH

4. A calculated amount of 13.2 mmol of sodium borohydride was slowly added to the mixture.

5. The resultant mixture was subjected to high-speed stirring for an hour for the metal salts to adhere to the surface of MWCNTs. After that, the mixture was refluxed for 3 h at 160 °C under a continuous flow of nitrogen; it was then left to cool down and then washed with ultra-pure water.

6. Finally, the mixture was then filtrated and the residue (PtRu/MWCNT nanoparticle) was oven-dried at 60 °C overnight and PtRu/MWCNT catalyst will be obtained

3.2.2.3 IMPREGNATION METHOD

1. In an impregnation method process the same calculated amount of the precursor salts, 0.07772mmol of $H_2PtCl_6 \cdot 6H_2O$ and 0.1544 mmol of $RuCl_3$ and the catalyst support(75mg), multi-walled carbon nanotubes with ethylene glycol mixture of 1:1 ratio were dispersed in a single beaker.

2. Followed by ultrasonic blending for 15 mins.

3. The reduction of the precursor salts $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3$ to the binary electrocatalyst (PtRu/MWCNT) was also achieved with 25 ml of 0.2M solution of $NaBH_4$.

4. The resultant mixture was subjected to high-speed stirring for an hour for the metal salts to adhere to the surface of MWCNTs

5. Finally, the mixture was then filtrated and the residue (PtRu/MWCNT nanoparticle) was oven-dried at 60 °C overnight and PtRu/MWCNT catalyst will be obtained.

3.2.2.4 HEAT TREATMENT OF THE BINARY PtRu/MWCNT CATALYSTS

The modified polyol process synthesized PtRu/MWCNT binary catalysts were heat treated at different temperatures under controlled temperatures. The heat treatment of the catalysts affects their morphology and activity, as well as their uniform distribution on the catalytic support. The tube furnace was pre-heated to the desired temperature. An alumina boat containing the catalyst was placed into the tube furnace's center. The catalyst was heated for 3 hours at different target temperatures of 250^0C, 350^0C, and 450^0C while nitrogen flowed at a rate of 5ml/min simultaneously. When the heating time was up, the tube was cooled down with the nitrogen gas still constantly flowing at a rate of 5ml/min, and the catalyst was removed from the furnace.

3.2.2.5 MICROWAVE ASSISTED MODIFIED POLYOL METHOD TO PREPARE BINARY PtRu/MWCNT CATALYST

1. 75mg of MWCNTs was added to 60ml ethylene glycol (EG) for ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRu (1:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6.6\ H_20$ and 0.1544mmol of $RuCl_3$ precursors were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs.

5. In the absence of a magnetic stirrer, the reaction mixture was moved into a sealed Teflon vial, which was then placed into a SiC sleeve and placed into a SOLV Model Multiwave Anton Parr Reaction System (Anton Parr, Graz, Austria), with the infrared sensor temperature probe placed into the reaction mixture to measure and monitor the reaction temperature. At a power of 800 W, the ramping time was set at 20 minutes to heat the reaction mixture from room temperature to the appropriate temperature. The reaction was kept at the desired temperature for 3 minutes after ramping up to it. Through a fan-induced connective flow in the microwave system, the microwave system automatically cools down to 55ºC in about 21 minutes after attaining the target time. The microwave is equipped with a revolving plate that rotates the Teflon vial at 2 rpm throughout the process. The reaction mixture in the Teflon vial was transferred to a centrifuge tube and spun for 30 minutes at 4500 rpm after cooling. The micro-Anton Parr microwave reactor, set to 800W, produced a PtRu/MWCNT paste, which was diluted with ultra-pure water and filtered. After that, the PtRu/MWCNT electrocatalyst was washed and oven-dried overnight at 60 °C.

3.2.2.6 PREPARATION OF TERNARY CATALYST PtRuIr/MWCNT, PtRuMo/MWCNT and PtRuW/MWCNT

The ternary catalysts were prepared using the microwave assisted method.

a. PREPARATION OF PtRuIr/MWCNT

1. 75mg of MWCNTs was added to 60ml ethylene glycol (EG) for ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRuIr (1:2:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6.6\ H_20$, 0.1544mmol of $RuCl_3$ and 0.1544mmol of $IrCl_3.\ xH_2O$ precursors were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs.

5. In the absence of a magnetic stirrer, the reaction mixture was moved into a sealed Teflon vial, which was then placed into a SiC sleeve and placed into a SOLV Model Multiwave Anton Parr Reaction System (Anton Parr, Graz, Austria), with the infrared sensor temperature probe placed into the reaction mixture to measure and monitor the reaction temperature. At a power of 800 W, the ramping time was set at 20 minutes to heat the reaction mixture from room temperature to the appropriate temperature. The reaction was kept at the desired temperature for 3 minutes after ramping up to it. Through a fan-induced connective flow in the microwave system, the microwave system automatically cools down to 55ºC in about 21 minutes after attaining the target time. The microwave is equipped with a revolving plate that rotates the Teflon vial at 2 rpm throughout the process. The reaction mixture in the Teflon vial was transferred to a centrifuge tube and spun for 30 minutes at 4500 rpm after cooling. The micro-

Anton Parr microwave reactor, set to 800W, produced a PtRuIr/MWCNT paste, which was diluted with ultra-pure water and filtered. After that, the PtRuIr/MWCNT electrocatalyst was washed and oven-dried overnight at 60 °C.

b. PREPARATION OF PtRuMo/MWCNT

1. 75mg of MWCNTs was added to 60ml ethylene glycol (EG) for ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRuMo (1:2:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6.6\ H_20$, 0.1544mmol of $RuCl_3$ and 0.1544mmol of $MoCl_3$ precursors were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs.

5. In the absence of a magnetic stirrer, the reaction mixture was moved into a sealed Teflon vial, which was then placed into a SiC sleeve and placed into a SOLV Model Multiwave Anton Parr Reaction System (Anton Parr, Graz, Austria), with the infrared sensor temperature probe placed into the reaction mixture to measure and monitor the reaction temperature. At a power of 800 W, the ramping time was set at 20 minutes to heat the reaction mixture from room temperature to the appropriate temperature. The reaction was kept at the desired temperature for 3 minutes after ramping up to it. Through a fan-induced connective flow in the microwave system, the microwave system automatically cools down to 55ºC in about 21 minutes after attaining the target time. The microwave is equipped with a revolving plate that rotates the Teflon vial at 2 rpm throughout the process. The reaction mixture in the Teflon vial was transferred to a centrifuge tube and spun for 30 minutes at 4500 rpm after cooling. The micro-

Anton Parr microwave reactor, set to 800W, produced a PtRuMo/MWCNT paste, which was diluted with ultra-pure water and filtered. After that, the PtRuMo/MWCNT electrocatalyst was washed and oven-dried overnight at 60 °C.

c. PREPARATION OF PtRuW/MWCNT

1. 75mg of MWCNTs were added to 60ml ethylene glycol (EG) for the ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRuMo (1:2:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6.6H_20$, 0.1544mmol of $RuCl_3$ and 0.1544mmol of WCl_4 precursors were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH was adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs.

5. In the absence of a magnetic stirrer, the reaction mixture was moved into a sealed Teflon vial, which was then placed into a SiC sleeve and placed into a SOLV Model Multiwave Anton Parr Reaction System (Anton Parr, Graz, Austria), with the infrared sensor temperature probe placed into the reaction mixture to measure and monitor the reaction temperature. At a power of 800 W, the ramping time was set at 20 minutes to heat the reaction mixture from room temperature to the appropriate temperature. The reaction was kept at the desired temperature for 3 minutes after ramping up to it. Through a fan-induced connective flow in the microwave system, the microwave system automatically cools down to 55ºC in about 21 minutes after attaining the target time. The microwave is equipped with a revolving plate that rotates the Teflon vial at 2 rpm throughout the process. The reaction mixture in the Teflon vial was transferred to a centrifuge tube and spun for 30 minutes at 4500 rpm after cooling. The micro-Anton Parr microwave reactor, set to 800W, produced a PtRuW/MWCNT paste, which was

diluted with ultra-pure water and filtered. After that, the PtRuW/MWCNT electrocatalyst was washed and oven-dried overnight at 60 °C.

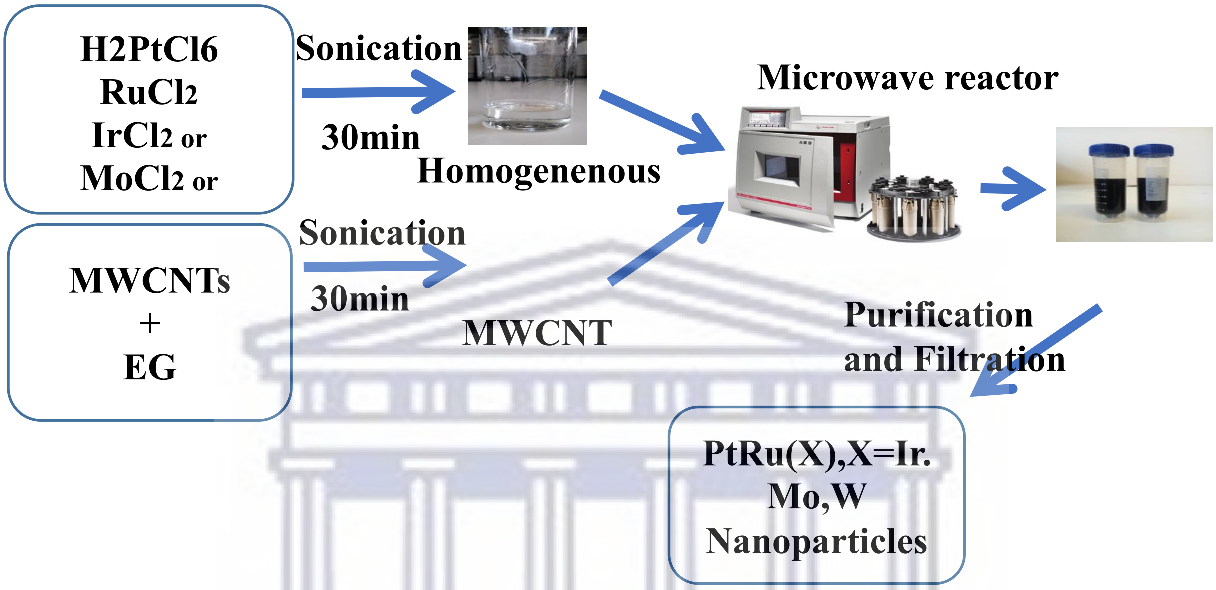

Figure 3. 1: Schematic diagram for the microwave assisted modified polyol method of catalyst preparation.

3.2.3 INK PREPARATION

1. A stock solution of 20% isopropanol and 0.02% Nafion is prepared by mixing 79.6 ml of ultrapure water, 20ml of isopropanol and 0.4ml of 5 wt. % Nafion solution in 100ml volumetric flask.
2. 10mg of the catalyst is measured into a 10ml vial and 5ml of stock solution is added; mixed through and sonicated for 1 hour.
3. The glassy carbon electrodes was polished with a 0.05 μm Al_2O_3 particle suspension on a moistened polishing cloth (Buehler, Micro-Cloth) in a “figure eight” pattern for four minutes to a mirror finish
4. The polished electrode is rinsed well with nanopure water and then dried at room temperature in air for at least 20 minutes before use.

5. A 0.02mg of the catalyst ink was then transferred via a syringe onto a freshly polished (mirror finish) Glassy Carbon (GC) electrode with a diameter of 5 mm (Single) having a geometric area of 0.196cm^2.

3.3 CHARACTERIZATION TECHNIQUES

The following physical and electrochemical methods were used to characterize the synthesized binary and Ternary catalysts.

For structural identification of the catalyst- 3 instruments were used

- High-resolution transmission electron microscopy (HRTEM)
- X-ray diffraction microscopy (XRD)
- Fourier Transmission Infrared (FTIR) spectroscopy

For elemental analysis

- Energy dispersive spectroscopy (EDS)

For electrochemical characterization 3 techniques were used

- Cyclic voltammetry (CV)
- Electrochemical Impedance Spectroscopy (EIS)
- Chronoamperometry (CA)

3.3.1 PHYSICAL CHARACTERIZATION

3.3.1.1 HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

Transmission electron microscopy is a microscopy technique in which a beam of electrons is sent through a specimen and produces a micrograph. The sample is usually an ultrathin layer of less than 100 nm in thickness or a grid suspension. The connection of the electrons with the sample as the beam passes through the sample produces a micrograph. The image is then centered on an imaging device, such as a fluorescent screen, a layer of photographic film, or a charge-coupled device sensor. A standard TEM is made up of a light source, a condenser lens, a stage for the specimen, an objective lens, and a projector lens [1].

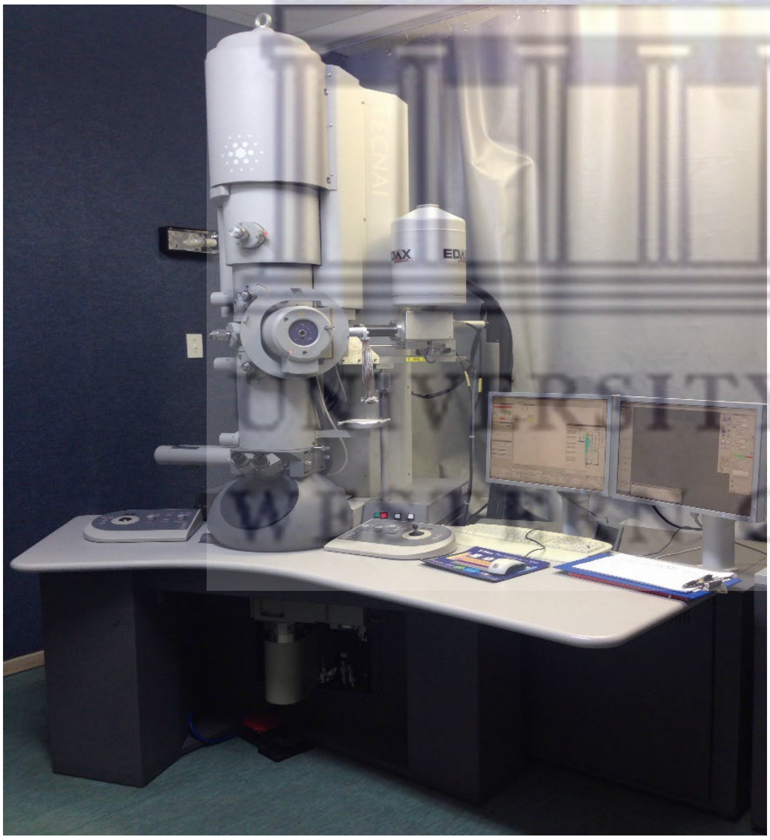

Figure 3. 2**:** Transmission Electron Microscopy (TEM) [2]

Because electrons have a shorter de-Broglie wavelength, transmission electron microscopes are suited for imaging at better resolution. This allows the sensor to detect minute details, such as a single atom section [3]. In the physical, chemical, and natural sciences, transmission electron microscopy is a critical analysis strategy. TEMs are used in virology, contamination, nanotechnology, and semiconductor research, as well as virology, contamination, nanotechnology, and semiconductor research. TEM micrograph contrast is caused by the differential absorption of electrons by the material at lower amplifications due to contrasts in the arrangement or thickness of the material. Complex wave synergy alters the intensity of the image at higher amplifications, necessitating a careful study of the micrographs. In addition to typical absorption-based imaging, TEM may detect changes in chemical properties, crystal arrangement, electronic structure, and sample-driven electron stage shift using other interchangeable modes [4]. For this study, the TECNAI G2 F2O X-TWIN MAT 200 kV field emission TEM was used to look at the material. To make the material more conductive, a nickel grid was used to cover it, and the average imaging resolution was 1.5 nm.

Sample preparation:

Samples were prepared by drop-coating one drop of specimen solution onto a carbon-coated copper grid. This was then dried under a Xenon lamp for about 10 minutes, where the sample coated grids were analyzed under the microscope.

Instrumentation:

Transmission electron micrographs were collected using an FEI Tecnai G2 20 field-emission gun (FEG) TEM, operated in bright field mode at an accelerating voltage of 200 kV. Energy dispersive x-ray spectra were collected using an EDAX liquid nitrogen-cooled Lithium doped Silicon detector**.**

3.3.1.2 X-RAY DIFFRACTION (XRD)

A multipurpose X-ray diffractometer from Bruker, the D8-Advance, is used for the measurements of diffraction patterns. It is operated in a continuous θ-θ scan in locked-linked mode with Cu-K_α radiation. The sample is put on a glass slide in the middle of the sample holder and raised to the right height. The measurements follow a user-defined range in 2ϑ with an average step size of 0.034° in $2\ \theta$. A Lyn-Eye, a position-sensitive detector, is used to collect diffraction data at a typical step rate of 0.5 seconds, which is comparable to a scintillation counter's effective step rate of 92 seconds.

After choosing a set of potential elements from the periodic table, data is background-subtracted to phase analyze the diffraction pattern with zero background. The phases are found by comparing the peaks that were predicted and those that were seen. This is done until all of the phases have been found, up to the resolution of the results.

In a cathode ray tube, X-rays are produced in a conventional XRD analysis by heating the filament to produce electrons. By supplying voltage and hitting the target material with electrons, the generated electrons are then accelerated in their direction. Characteristic X-ray spectra are created when the electrons have enough energy to knock the target material's inner shell electrons loose. With a CuK_α radiation of 1.5418 Å, copper is typically the target material utilized for single-crystal diffraction. The sample will be exposed to collimated X-rays. The intensity of the reflected X-rays is measured while the sample and detector spin. When the conditions are by Bragg's law, constructive interference is produced by the interaction of the incident rays with the sample, and a peak in intensity results (equation 3.1). This X-ray signal is captured by a detector, which also processes it. After that, the signal is changed into a count rate and sent to a printer or computer [5].

$$n\lambda = d\sin\theta \tag{3.1}$$

Bragg's law requirements are satisfied by various d-spacing in polycrystalline materials by changing the angle. A pattern that is typical of the sample with a mixture of different phases is created by plotting the angular positions and intensities of the resulting diffracted radiation peaks. The result is a diffractogram after each pattern is added. Based on the X-ray diffraction principle [6], we can now learn a lot about the structure, physics, and chemistry of the material being studied.

As mentioned above, the Scherrer equation can be used with XRD to objectively figure out the average size of particles:

$$D = 0.9\,\lambda / \beta\cos\theta \tag{3.2}$$

The particle size is represented by D, the shape factor is 0.9, λ the X-ray wavelength, β the peak width at half peak height (in radians), and θ represents the angle of reflection [7]. The broadening of a specific peak in a diffraction pattern connected to a specific planar reflection from inside the crystal unit cell is measured to determine the crystal size. The relationship between particle size and an individual peak's half-width at half maximum is inverse. Generally speaking, the more crystalline the sample is, the narrower and stronger the peak. Small particle size and an amorphous substance are typically linked to a broad peak [8]. The X-ray diffractometer employed in this work, a BRUKER AXS DS Advance diffractometer at Ithemba Labs Cape Town, operates at 45 kV and 40 mA, with a step size of 0.028^0 and 2θ values ranging from 10–80^0C.

Figure 3. 3**:** Advance diffractometer at Ithemba Labs Cape Town, operates at 45 kV and 40mA

Parameters:

Tube voltage: 40kV

Tube current: 40mA

Variable slits: V20 variable slit

2ϑ Range available: 0.5° to 130° ; see your data (angles in degrees)

Increment Δ2ϑ: (0.034°) most of the time; see your data

Measurement time: 0.5 sec/step most of the time.

Sample Preparation

The sample was crushed into a fine powder. A spatula was used to level the catalyst powder in a sample holder. The sample was placed in the Xray diffractometer. Diffraction patterns were gathered throughout a two-angle range of 10^0C to 80^0C. The mineral was identified by comparing it to available d-spacing data and significant peaks from the International Centre for Diffraction Data and Bruker's EVA software.

Instrumentation:

Manufacturer: BRUKER AXS (Germany)

Diffractometer: **D8 Advance**

Measurements: continuous θ-θ scan in locked coupled mode

Tube: Cu-Kα radiation ($\lambda K\alpha_1$=1.5406Å)

Detectors: LynxEye (Position sensitive detector)

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3.3.1.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In the nineteenth century, infrared light was first identified. Since then, researchers have created several methods for using infrared light. By measuring the amount of infrared radiation that is absorbed by the functional groups of molecules, scientists utilize infrared absorption spectroscopy to ascertain the structure of molecules. The vibrational spectrum of molecules is the infrared spectrum [9]. Infrared light causes sample molecules to selectively absorb radiation of particular wavelengths, changing the dipole moment as a result. As a result, the sample molecules' vibrational energy levels shift from excited to ground. The frequency of the absorption peak is determined by the vibrational energy gap. The variety of absorption peaks is associated with the molecule's extensive range of vibrational flexibility. The likelihood of energy level transitions and the shift in the dipole moment both affect the absorption peaks' strength. After examining the infrared spectrum,

By examining a molecule's spectrum, you can quickly discover a lot about its structure. The majority of molecules are infrared active, except a small number of diatomic molecules like O_2, N_2, and Cl_2, which have zero dipole change in their vibration and rotation. Infrared absorption spectroscopy is much more useful because it can accurately measure any gas, liquid, or solid [10, 11].

The near-infrared (12800 – 4,000 cm-1), mid-infrared (4000 – 200 cm-1), and far-infrared (12800 – 6,000 cm-1) regions of the infrared spectrum can be distinguished (50 thousand cm-1). The range between 4000 and 400 cm-1 is the one most frequently utilized in infrared absorption spectroscopy because it contains the highest number of natural compounds and inorganic ions that absorb radiation [12].

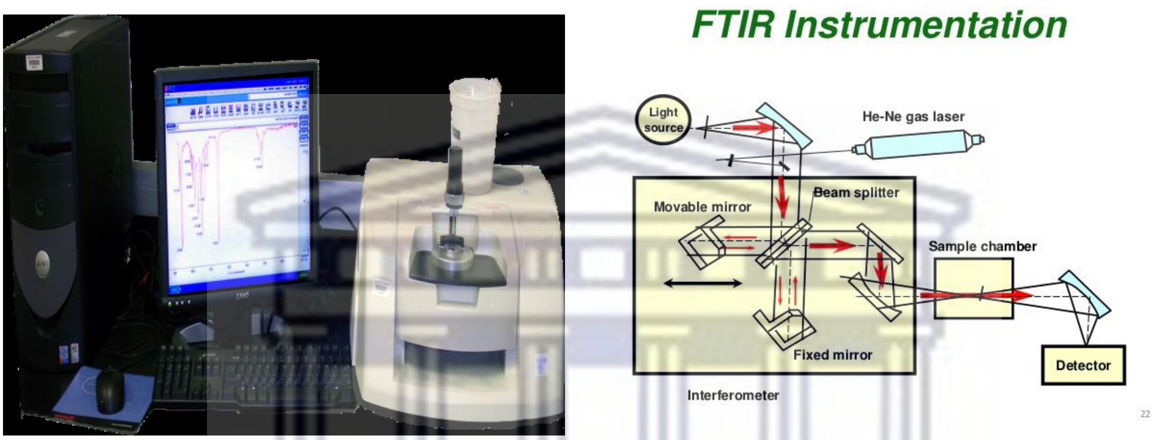

Figure 3. 4: Schematic 1) and 2) working station of FTIR spectroscopy [13, 14]

Sample Preparation

The functionalized MWCNT samples were ground with potassium bromide, KBr. The resulting mixture was directly placed inside the FTIR spectrophotometer. The probe was inserted into the sample, which was held in place by the sample holder.

Instrumentation

Instrument Name	Perkin Elmer spectrum 100 series FT-IR Spectrometer
Scan Range	400 to 4000 cm^{-1}(Funcntional group regions.)

3.3.2 ELEMENTAL ANALYSIS

3.3.2.1 ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDX)

The quantitative elemental analysis method known as Energy Dispersive X-ray (EDX) microanalysis, which is related to electron microscopy, identifies the presence of elements in specimens by measuring the emission of unique X-rays [15]. Several emissions, including X-rays, are produced when an electron beam strikes a sample surface. The distinctive x-rays of each element are split into an energy spectrum using an energy-dispersive (EDS) detector. The EDS system software then examines the energy spectrum to determine the abundance of each element [16].

Energy dispersive X-ray can be used to create element composition maps over a much greater raster area and to determine the chemical composition of materials down to a few microns in size. EDX systems come equipped with a sensitive x-ray detector, a liquid nitrogen dewar for cooling, and software to gather and analyze energy spectra. In the sample chamber of the primary instrument, a long arm with a liquid nitrogen cooling system houses the detector. The most common detectors are made of Si (Li) crystals that operate at low voltages to increase sensitivity.

The energy of incoming x-rays is absorbed by a detector crystal by ionization, creating free electrons that become conductive and lead to an electrical charge bias [17]. Therefore, x-ray absorption transforms the energy of individual x-rays into electrical voltages of corresponding size; the electrical pulses correspond to the element's specific x-rays. Most frequently, an EDX spectrum is shown as a graph of x-ray counts vs energy (in keV). Energy peaks in the sample are correlated with the different elements. Usually tiny and simple to fix, there are multiple peaks due to a number of causes. Iron, for example, frequently exhibits significant K-α and K-β peaks. It may be challenging to discern between low-abundance elements' x-ray peaks and background radiation [18].

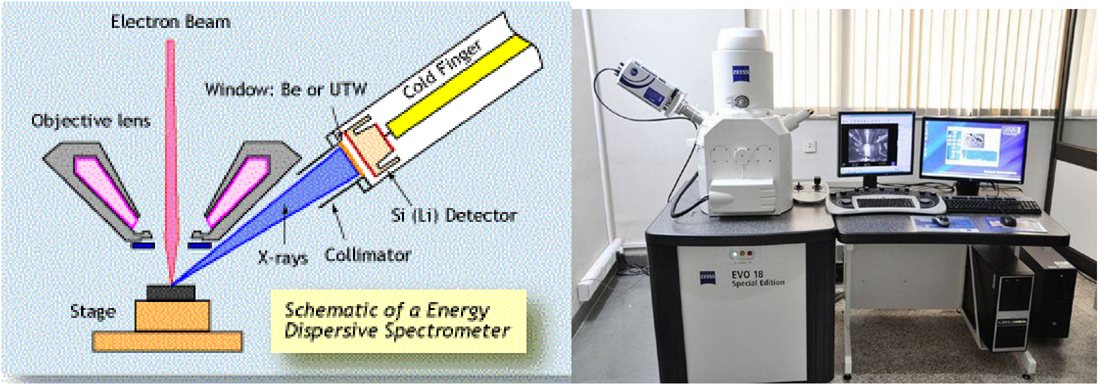

Figure 3. 5**:** 1) Energy-Dispersive X-ray spectroscopy (EDX) work stationand 2) Schematic of Energy Dispersive X-ray Spectrometer [19]

Sample Preparation

The catalytic samples' conductive powders were spread on carbon stick tabs and put on an aluminum stub holder. The holder was then inserted into the spectrometer.

Instrumentation

In this experiment, an Oxford X-Max silicon drift EDS detector was used. This detector makes high-resolution EDS spectra at low beam currents with good count rates.

Operational Parameters

Parameter	**Setting**
Accelerating voltage	25keV
Tilt Angle	0°
Aperture	0.4mm
Resolution	3nm
Working distance	15mm
Magnification	50k

3.3.3 ELECTROCHEMICAL CHARACTERIZATION

Electrochemistry is the study of the connection between electric and chemical events [20]. It focuses on two areas: electrolysis, which involves the conversion of chemical compounds through the passage of an electric current; and electrochemical power sources, which involve the conversion of chemical reaction energy into electricity. Electrochemistry is a useful tool for examining electron transfer parameters. The term "heterogeneous method" refers to electron transport between a substrate and a solution species. In contrast, when electron transfer occurs between two species, either of which may be in solution, the reaction is referred to as homogenous. So, electrochemistry is the study of the structures and methods used at the interface between an electronic conductor (an electrode) and an ionic conductor (an electrolyte) or between ionic conductors [21].

In this study electrochemical measurements were carried out at ambient temperatures using a three-electrode configuration, which includes a working electrode, a counter electrode and a reference electrode. An Ag/AgCl electrode as a reference electrode and a Pt foil of a large area as a counter electrode were used. The working electrode was a glassy carbon disc (5 mm in diameter with a geometric area of 0.196 cm^2) covered with a thin layer of catalyst of fine film. Before the experiment, the electrode substrate was pre-treated by polishing it with a 0.05µm Al2O3 particle suspension on a moistened microcloth. The electrolyte used was 0.5M perchcloric acid solution.

Electrochemistry is an interdisciplinary subject with roots in chemistry and physics, but it also has connections to engineering and biochemistry and biology. Electrochemistry has found applications in a wide range of fields, including analytical electrochemistry, environmental electrochemistry [22], electrochemistry of glasses [23], ionic liquids electrochemistry, micro-electrochemistry, surface electrochemistry, and technical electrochemistry, which includes several subtopics such as batteries and energy storage [24], and corrosion and corrosion inhibition. This dissertation reports about current measurements, voltammetry, and a number of electrochemical techniques, such as cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS).

Figure 3. 6**:** An electrochemical working station showing autolab (galvanostat) and the three Electrodes electrochemical cell assembly [25]

3.3.3.1 CYCLIC VOLTAMMETRY (CV)

The most versatile electroanalytical approach for the investigation of electroactive substances is cyclic voltammetry. Because of its ease of measurement and versatility, it is widely used in a variety of scientific domains, including electrochemistry, organic chemistry, inorganic chemistry, and biochemistry. In an electrochemical investigation of a substance, biological material, or electrode surface, cyclic voltammetry is frequently the first technique used. The capacity of cyclic voltammetry to immediately observe the redox reaction behaviour across a wide potential range is what gives it its current. The voltammograms that are made are like traditional spectra in that they send information based on the potential difference (voltage) per unit time that is being scanned [26].

The potential of a working electrode is altered linearly with time in cyclic voltammetry, starting at a potential where no electrode reaction occurs and progressing to potentials where a solute is reduced or oxidized. The direction of the linear sweep is reversed after passing over the potential regions where one or more electrode reactions occur, and the electrode reactions of the intermediates and products created during the forward scan may often be observed. The experiment's time scale is determined by the scan rate. In the presence of a supporting electrolyte, cyclic voltammetry is commonly performed with a three-electrode system consisting of a working electrode, a reference electrode, and a counter electrode. The reference electrode measures the potential of the working electrode without passing current through it, whereas the counter electrode enables current to pass through it. If oxidation occurs at the working electrode, reduction using the same magnitude of current is sustained at the counter electrode, resulting in no current flow between the working and reference electrodes (a high input electrical resistance), allowing us to reliably follow changes in working electrode potential. This is not achievable in a two-electrode system.

A conventional hydrogen electrode, saturated calomel electrode, or silver electrode chloride can be used as the reference electrode. The working electrode is usually a glassy carbon electrode coated with the catalyst being researched, whereas the counter electrodes can be gold, platinum, or carbon. The supporting electrolyte is present to prevent charged reactants and products from migrating [27]. It's usually utilized to get a better understanding of electrolytic action.

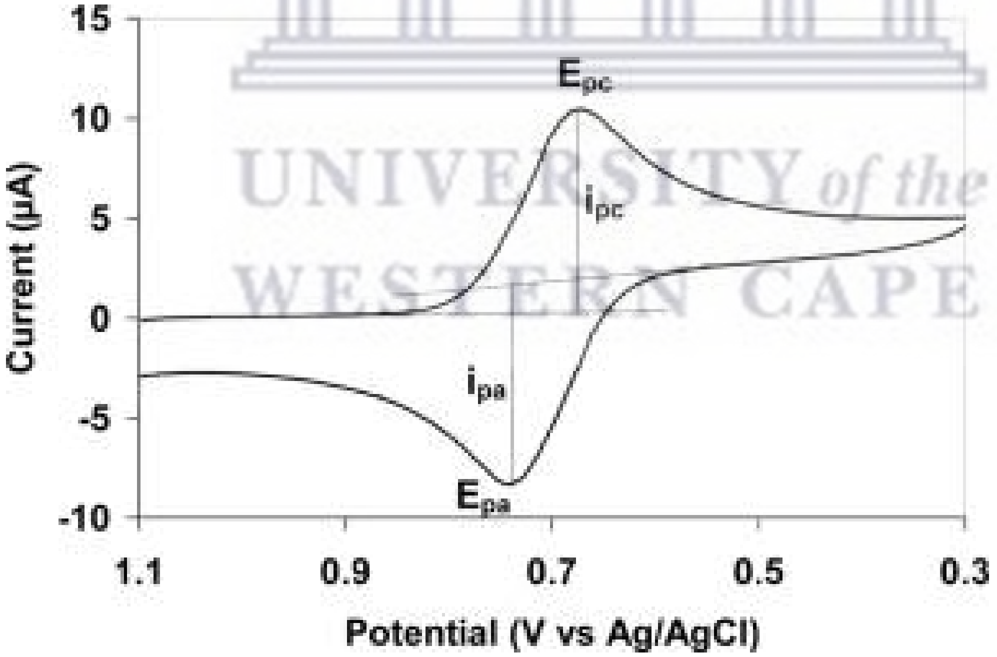

Figure 3. 7**:** Typical cyclic voltamgramm showing anodic and cathodic peak voltages and peak currents for a reversible redox process.[28]

The peak area of the adsorption peak of the electrocatalysts in the CV was used to determine the electroactive surface area of the catalysts using the equation 7[24]. ECSA is a characteristic that is used to determine the prepared catalyst's electro-catalytic activity. The ECSA is a measurement of the catalysts electro-active surface, derived using the equation:

$$ECSA = \frac{Q}{210\mu C/cm2.m.Ag} \qquad 3.3$$

where Q is the charge from the adsorption peak of cyclic voltammogram in Coulomb taking within in negative potential region -0.2 V to 0.08 V in the forward scan, m is the working electrode Pt loading in g cm^{-2}, Ag is the geometric surface area of the electrode (5 mm in diameter, Ag = 0.196 cm^2) and 210µCcm^{-2} is the value for the charge of full coverage for clean polycrystalline Pt monolayer [29]

The Autolab M204 was used in this study, and it has a potential range of +/- 10 V, compliance voltage of +/- 20 V, maximum current of +/- 400 mA, current ranges of 100 mA to 10 nA, potential accuracy of +/- 0.2 percent, potential resolution of 3 V, current accuracy of +/- 0.2 percent, current resolution 0.0003 percent (of current range), input impedance of > 100 GOhm, and potentiostat bandwidth of 1 MHz.

3.3.3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Electrochemical impedance spectroscopy (EIS) is a useful approach for identifying the electrical resistances in a fuel cell stack. AC impedance tests can help determine the kinetic, ohmic, electrolytic, and diffusion layer resistances, as well as the machine's delivery constraints. The reaction is an alternating current (AC) sign of the same frequency with a possible phase shift and amplitude trade, and the technique uses a small sinusoidal perturbation potential at one or more frequencies. The AC is imposed on top of the DC generated by the fuel cell in a few-dimensional system, and the voltage is recorded instead of the current. A mathematical method is utilized to calculate the impedance based on the recorded response. An electrochemical impedance spectrum is obtained by repeating this process at various frequencies. An EIS is a non-invasive approach for varying the fuel cell's current or voltage by a percentage. The magnitude of the variations is determined by the AC signal's peak-to-peak current and the fuel cell's impedance at each frequency [30]. An electronic load, a function generator, and a computer are used to achieve the AC-Impedance measurement. This is also the same technique that may be used to create polarization or IC curves for a fuel cell. Because it tests every frequency, EIS is effective in defining quick and gradual delivery processes. This test indicates mass transfer resistance, electron transfer resistance at particular stages of electrochemical reactions, and ionic resistance through the membrane. This information can then be used to assess the various impedances found within the gas cell [31].

The EIS method is a variation of the high-frequency resistance (HFR) method, although it takes two different ways. The HFR approach analyses only the real components of the impedance and uses a single frequency. The EIS uses a frequency response analyzer to calculate the fuel cell's complex impedance (real part (Z') and imaginary part (Z")) by measuring a wide range of frequencies and monitoring the subsequent fluctuations in value and segment of the cell voltage and current. Except for setting the characteristic generator frequency, the test is straightforward. The most widely used approach for differentiating fuel cell losses is electrochemical impedance spectroscopy [32].

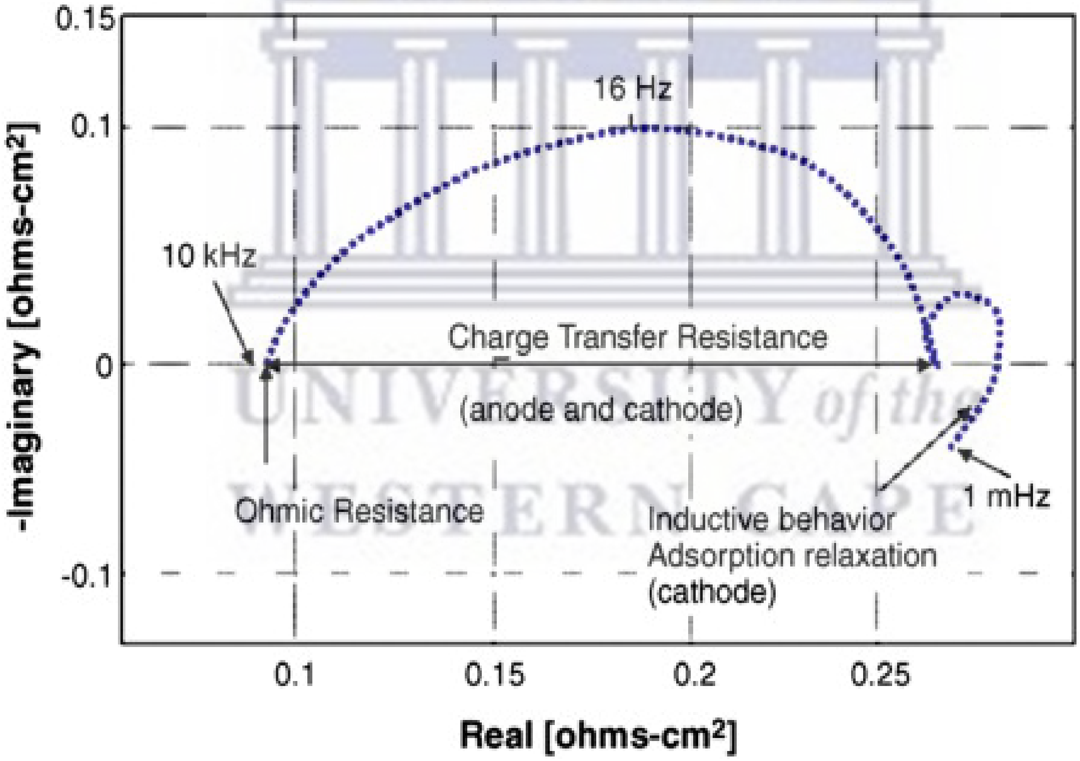

Figure 3. 8**:** Electrochemical Impedance Spectroscopy (EIS) curve [34]

The ability of a circuit to resist the flow of electrical current is measured by its impedance. The frequency-dependent resistance to current flow of a circuit element is referred to as impedance (resistor, capacitor, inductor, etc.). Impedance is based on an AC current with a certain frequency expressed in Hertz (cycles per second). Impedance is described by the equation below.

Impedance: $Z\omega = E\omega / I\omega$ (3.4)

Where E represents frequency-dependent potential and I represents frequency-dependent current. EIS has a much higher information content than DC techniques or single frequency measurements, and it can distinguish between two or more electrochemical reactions, identify diffusion-limited reactions, such as diffusion through a passive film, and provide data on the capacitive behavior of the system. Components within a constructed device can be tested using the device's own electrodes, providing information on the electron transfer rate of reaction. Corrosion of metals, adsorption and desorption on electrode surfaces, electrochemical synthesis of materials, catalytic reaction kinetics, label-free detection sensors, and ion mobility in energy storage devices such as batteries and supercapacitors are some of the applications [33]. The Autolab M204 was used in this study, and it has a potential range of +/- 10 V, compliance voltage of +/- 20 V, maximum current of +/- 400 mA, current ranges of 100 mA to 10nA, potential accuracy of +/- 0.2 percent, potential resolution of 3 V, current accuracy of +/- 0.2 percent, current resolution 0.0003 percent (of current range), input impedance of > 100 GOhm, and potentiostat bandwidth of 1 MHz.

3.3.3.4 CHRONOAMPEROMETRY

The potential of the working electrode is stepped in chronoamperometry, and the current faradaic processes that ensue are measured. Chronoamperometry is an electrochemical technique that creates high-charging currents that, like any RC circuit, decrease exponentially with time. Almost always, the faradaic current resulting from electron transfer is the parameter of interest [35]. Chronoamperometry was utilized to test the catalyst's stability in this study.

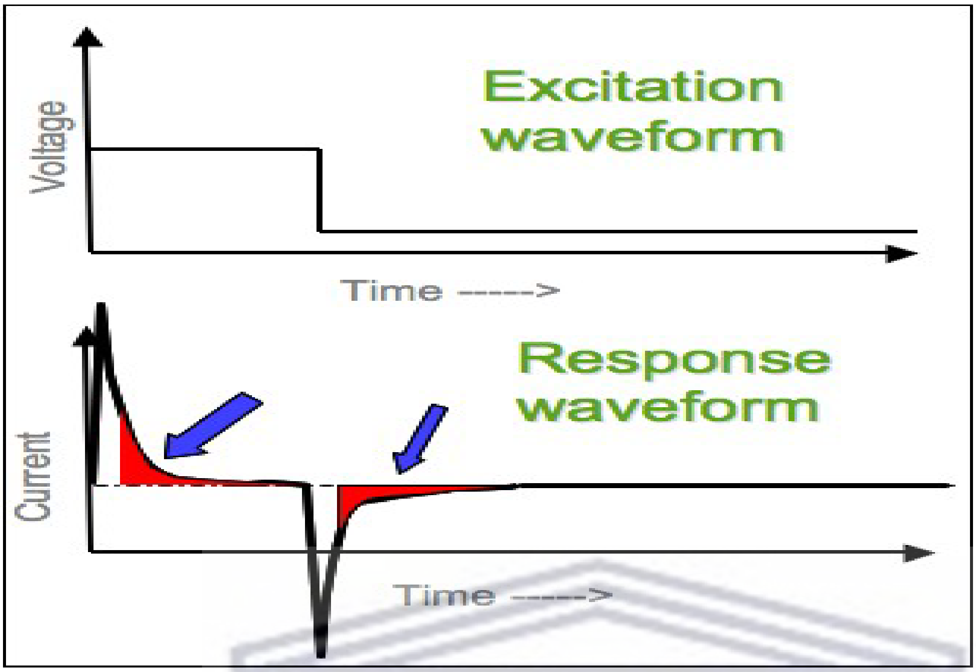

Figure 3. 9**:** Double-pulsed chronoamperometry waveform showing integrated region for charge determination [38]

In Chronoamperometry, the generate current-time dependence is monitored. The current-time curve reflects the change in the concentration gradient in the place of the surface. This includes a sluggish expansion of the diffusion layer related to the depletion of the reactant as time progresses, consequently the current decays with time (at a planar electrode). The current flows at any time after application of the potential step will obey the Cottrell equation.

$$i(t) = nFAcD^{1/2}/(nt)^{1/2} = Kt^{-1/2} \tag{3.5}$$

The number of electrons, Faraday constant, surface area, concentration, diffusion coefficient, and time are represented by n, F, A, c, D, and t, respectively. Chronoamperometry is frequently used to determine the diffusion coefficient of electroactive species or the working electrode's surface area. It can also be used to investigate the mechanisms of electrode processes [36, 37]. The Autolab M204 was used in this study, and it has a potential range of +/- 10 V, compliance voltage of +/- 20 V, maximum current of +/- 400 mA, current ranges of 100 mA to 10 nA, potential accuracy of +/- 0.2 percent, potential resolution of 3 V, current accuracy of +/- 0.2 percent, current resolution of 0.0003 percent (of current range), input impedance of > 100 GOhm, and potentiostat bandwidth of 1 MHz.

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CHAPTER FOUR

RESULTS AND DISCUSSIONS ON CATALYST SYNTHESIS METHODS TO DEVELOP BINARY CATALYSTS, PtRu/MWCNT

ABSTRACT

This chapter reports on various catalyst synthesis methods (impregnation, polyol, modified polyol and microwave-assisted modified polyol methods) to determine which method would result in the most electrochemically active platinum–ruthenium (PtRu) electrocatalyst supported on multi-walled carbon nanotubes (MWCNTs) for methanol oxidation reaction in an acidic medium. Different techniques were used to characterise the synthesised catalysts, including the high-resolution transmission electron microscope used for morphology and calculating particle sizes, and X-ray diffraction for determining crystalline sizes while Energy dispersive analysis Spectroscopy, EDS was used to determine elemental compositions. The electroactive catalyst surface area, ECSA of the electrocatalysts was determined using cyclic voltammetry (CV), while the electroactivity, electron kinetics and stability of the electrocatalysts towards methanol oxidation were evaluated using CV, electrochemical impedance spectroscopy and chronoamperometry, respectively. The microwave-assisted modified polyol method produced the PtRu/MWCNT electrocatalyst with the most enhanced electrocatalytic activity compared to other PtRu/MWCNT catalysts produced by the impregnation, polyol and modified polyol methods.

Keywords: Methanol oxidation; catalysts; multi-walled carbon nanotubes; electrocatalytic activity

4.0 INTRODUCTION

Catalyst synthesis methods have an influence on mean particle size, particle size distribution, the bulk and surface of catalysts' composition, the oxidation state of catalysts, the extent of catalyst alloying, the distribution of catalyst crystal surfaces and catalyst morphology [1,2], and hence on the catalytic activity of the metal catalysts [3]. The standard by which high-performance catalysts are evaluated includes a uniform composition in the entire nanoparticles, a complete alloying degree, a narrow nanoscale size distribution and high dispersion on carbon support [4]. Various methods for the synthesis of fuel cell catalysts have been reported in the literature [5], including micro-emulsion, sputtering and co-precipitation methods. In this study we report on the synthesis of catalysts using the impregnation, polyol, modified polyol and microwave-assisted modified polyol methods.

a. Impregnation method

The impregnation approach is frequently utilised for the synthesis of Pt-based catalysts. It is a straightforward chemical preparation process for catalyst synthesis that can create tiny particles in the 3–7nm range with regulated loading [5,6]. The impregnation method for the synthesis of platinum–ruthenium (PtRu) includes an impregnation step in which Pt and Ru precursor salts are mixed with the support material, which is typically high-surface area porous or nanostructured carbon and penetrates into pores. The catalyst support aids in the penetration and wetting of the precursor and the carbon support confines the particle size growth during the reduction step. The chemical reduction can be carried out in the liquid phase with a reducing agent such as $Na_2S_2O_3$, $NaBH_4$, $Na_4S_2O_5$, N_2H_4 or formic acid, or in the gas phase with a reducing agent such as a flowing hydrogen stream at elevated temperatures. The difficulty in adjusting nanoparticle size and distribution is a key limitation of the impregnation process [6,7]. It has been noted that impregnated catalysts have a tendency to generate inhomogeneous agglomerations of active species at the support boundary, resulting in large-sized particles [1].

Other difficulties include the use of chloride precursors, which could result in chloride poisoning and decreased catalytic activity and stability of the chloride-salt-produced catalyst. Metal nitrate/nitrite salts such as $Pt(NH3)_2(NO2)_2$ and $RuNO(NO_3)_x$ [8], carbonyl complexes such as $Ru_3(CO)_{12}$ [9] and metal sulphite salts such as $Na_6Pt\ (SO3)_4$ and $Na_6Ru(SO_3)_4$ [10] as metal precursors for Pt and Ru, respectively, have been investigated for impregnation methods that could use chloride-free precursors. When compared to the traditional Cl-containing route, these chloride-free pathways provide improved dispersion and catalytic activity [5]. In this chapter we report on an impregnation method where $NaBH_4$ was used as the reducing agent and ethylene glycol (EG) as the solvent.

b. Polyol reduction method

The polyol method includes the following common steps: 1) preparation of Pt-containing colloids; 2) deposition of the colloids onto the support; and 3) chemical reduction of the mixture. The synthesis occurs in an organic or aqueous medium where the metal precursor is reduced chemically in the presence of a protective agent (i.e. NR41, PPh_3, PVP, SB12 or PVA). Other colloid methods using several reducing agents, organic stabilisers or shell-removing approaches have also been developed in recent years. The catalyst is supported with a catalyst support to enhance the surface area and the dispersion of the catalyst. To achieve a limited size distribution, the colloidal metal nanoparticles are stabilised by steric hindrance or electrostatic charges. Coating the metal core with organic chain molecules can offer steric stability [11,12]. The aggregation of charged colloids or adsorbed ions is limited by the electrostatic repulsion of similar charges. The use of protective agents, which may influence the catalytic activity of the nanoparticles, poses a problem for the polyol process, but it may be removed by washing in a suitable solvent or breakdown at temperatures in an inert atmosphere. There are also other challenges facing the polyol method, such as that it is time-consuming, complex and expensive, which cause difficulty in terms of scaling up. The colloidal method prepares catalysts with nanoparticle size and a narrow size distribution.

The polyol method that was employed in this study has been extensively explored as a preparation method for Pt [6, 13]. In this chapter we report on a polyol method where the resultant mixture of a calculated amounts of the precursor salts and Ethylene glycol was subjected to high-speed stirring for an hour for the metal salts to adhere to the surface of MWCNTs. After that, the mixture was refluxed for 3 h at 160 °C under continuous flow of nitrogen; it was then left to cool down and then washed with ultra-pure water. Finally, the mixture was then filtrated and the residue (PtRu/MWCNT nanoparticle) was oven-dried at 60 °C overnight and PtRu/MWCNT catalyst was obtained.

c. Modified polyol reduction method

Fievet et al. [14] pioneered the use of EG as both a solvent and a reducing agent. They found that EG may support colloidal metal particles in solution, resulting in a well-distributed solution. EG has a relatively high viscosity, and therefore it prevents Pt from being delivered to reaction sites too quickly, resulting in reduced Pt particle sizes [15]. This method is called the modified polyol method [16]. The modified polyol method is able to effectively synthesise very small and well-dispersed metal nanoparticles [2]. However, the synthesis parameters such as the water: EG ratio, the concentration of EG and the pH of the solution have a great effect on the characteristics of the results [2]. Bimetallic catalysts, metal oxides and metal sulphides with narrow particle size distributions, controlled compositions and alloy structures have also been effectively prepared using the modified polyol technique [17]. The modified polyol approach, which uses EG as a reducing agent and solvent, was also used to make catalysts in this study. EG was utilised as both a reducing agent and a solvent for the Pt and Ru precursors in this method. The solution of EG, Pt and Ru precursor salts was heated to 120–170 °C during the reduction phase. EG is decomposed in this step, resulting in the reducing species (CH3CHO-acetaldehyde, Eq. (1)) [18].

$$CH_3OCH_2OH \rightarrow CH_3CHO + H_2O \qquad (1)$$

$$2CH_3CHO + (PtCl_6) + 6OH^- \rightarrow 2CH_3COO^- + Pt + 6Cl^- + 4H_2O \qquad (2)$$

As represented in Equation (2), acetaldehyde converts Pt ions into metallic Pt particles. The main feature of this polyol synthesis is that the acetate can act as a stabiliser for Pt and Ru colloids by forming chelate-type complexes via its carbonyl group. It is therefore unnecessary to use stabilisation agents to prevent PtRu particles from agglomerating. As a result of using modified polyol synthesis, carbon-supported catalysts with reduced noble metal sizes and a narrow size distribution are achieved.

d. Microwave-assisted modified polyol methods

The microwave synthetic approach was one of the methods employed in this study. A modified polyol method has been reported for this technique, with the deposition and reduction steps taking place in a microwave reactor. Microwave synthetic methodology has been utilised to manufacture catalysts because of its fast, uniform, homogeneous and instant heating environment, which resulted in rapid reduction and facilitated metal particle nucleation [19,20]. Microwave heating is a promising technology, with its applications rapidly growing due to its advantages over conventional heating, such as rapid volumetric heating, which increased reaction rates and shortened reaction time; however, to induce crystallisation, a post-synthesis heat treatment was required [3]. Under such conditions, a microwave-assisted synthesis method is an appropriate option, with the added benefits of narrow size distribution and high purity [4]. At high pH conditions for depositions, promising results were reported with an average Pt size of 2.7 nm. However, because the reaction takes place in a closed system, the pH cannot be controlled throughout the duration of the reaction, hence the entire scope of the reaction under these conditions is unknown [21].

In this study the microwave synthesis method was carried out as follows; In the absence of a magnetic stirrer, the reaction mixture was moved into a sealed Teflon vial, which was then placed into a SiC sleeve and placed into a SOLV Model Multiwave Anton Parr Reaction System (Anton Parr, Graz, Austria), with the infrared sensor temperature probe placed into the reaction mixture to measure and monitor the reaction temperature. At a power of 800 W, the ramping time was set at 20 minutes to heat the reaction mixture from room temperature to the appropriate temperature. The reaction was kept at the desired temperature for 3 minutes after ramping up to it. Through a fan-induced connective flow in the microwave system, the microwave system automatically cools down to 55ºC in about 21 minutes after attaining the target time. The microwave is equipped with a revolving plate that rotates the Teflon vial at 2 rpm throughout the process. The reaction mixture in the Teflon vial was transferred to a centrifuge tube and spun for 30 minutes at 4500 rpm after cooling. The micro-Anton Parr microwave reactor, set to 800W, produced a PtRu/MWCNT paste, which was diluted with ultra-pure water and filtered. After that, the PtRu/MWCNT electrocatalyst was washed and oven-dried overnight at 60 °C.

4.1 RESULTS AND DISCUSSION

4.1.1 Physical characterization of the prepared electrocatalysts

X-ray diffraction (XRD) and the high-resolution transmission electron microscope (HRTEM) were used to learn more about the catalyst structure. The XRD patterns were performed with the Bruker AXS D8 Advance equipment with Cu-K radiation and a wavelength of 1.5406 nm. With a scanning step of 0.035°, the Bragg angle range was $2\theta = 10–90°$. The instrumental contribution into peak profile characteristics was determined using a standard α--Al2O3 sample. A JEOL 2010 TEM system operating at 200 kV was used to obtain the HRTEM micrographs. The HRTEM samples were made by dispersing the carbon-supported electrocatalysts in ethanol and then casting a drop of the suspension onto a Cu-grid covered in carbon film for analysis. For each electrocatalyst, the particle size determined by HRTEM was obtained using Image J software over multiple areas.

4.1.2 XRD analysis

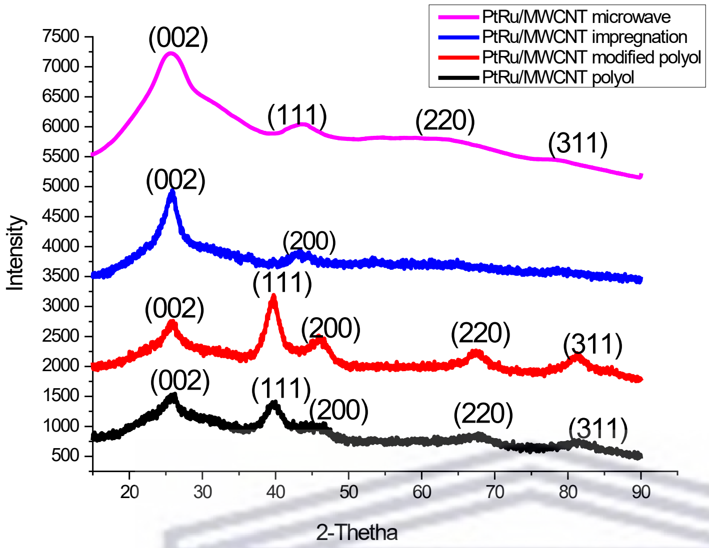

Figure 4. 1: XRD spectra of PtRu electrocatalysts supported on multi-walled carbon nanotubes (MWCNTs) prepared through the impregnation, polyol, modified polyol and microwave-assisted modified polyol methods

XRD measurements were performed to obtain the crystallographic information of the prepared catalysts. The XRD results presented in Figure 4. 1 indicate that all prepared metal catalysts presented a typical face-centered cubic crystallographic structure of Pt crystals. The Bragg angles indicate that varying bimetallic interactions or alloying occurred in the PtRu crystals due to different catalyst preparation methods. The diffraction peak for carbon is at about $2\theta = 25^0$. Other peaks are at 2θ values of 39.9^0, 46.21^0, 67.8^0 and 81.2^0, which are indexed to (111), (200), (220) and (311) planes of PtRu/MWCNT crystal structure, respectively. The strongest and sharpest diffraction peak for all four samples is at around $2\theta = 39.9^0$ indexed as (111) reflection of PtRu/MWCNT crystal planes prepared through the modified polyol and polyol methods, while the other characteristic PtRu/MWCNT diffraction peaks at 2θ of about 46.21^0, 67.8^0 and 81.2^0 corresponded to (200), (220) and (311), respectively. Similar results were also reported by Youngmin Kim et al [22] and Bohua Wu et al [23].

The crystalline size of the metal particles is calculated using Debye-Scherrer's equation, Kα/βCosθ

where K, Scherrer constant = 0.9, α, X-ray wavelength = 0.154 nm. B (2θ), the width of the diffraction peak (rad). From Table 1 the average particle size can be seen, with PtRu/MWCNT nanoparticles prepared through microwave-assisted modified polyol having the smallest crystalline size of 1.95 nm, followed by PtRu/MWCNT nanoparticles prepared through the modified polyol method with a crystalline size of 4.33 nm.

Table 4. 1: Properties of the PtRu electrocatalysts

PtRu electrocatalysts	**Crystalline size (nm)**	**Particle size (nm)**
PtRu/MWCNT modified polyol	4.33	4.14
PtRu/MWCNT polyol	6.75	6.51
PtRu/MWCNT impregnation	7.11	6.90
PtRu/MWCNT microwave	1.95	1.87

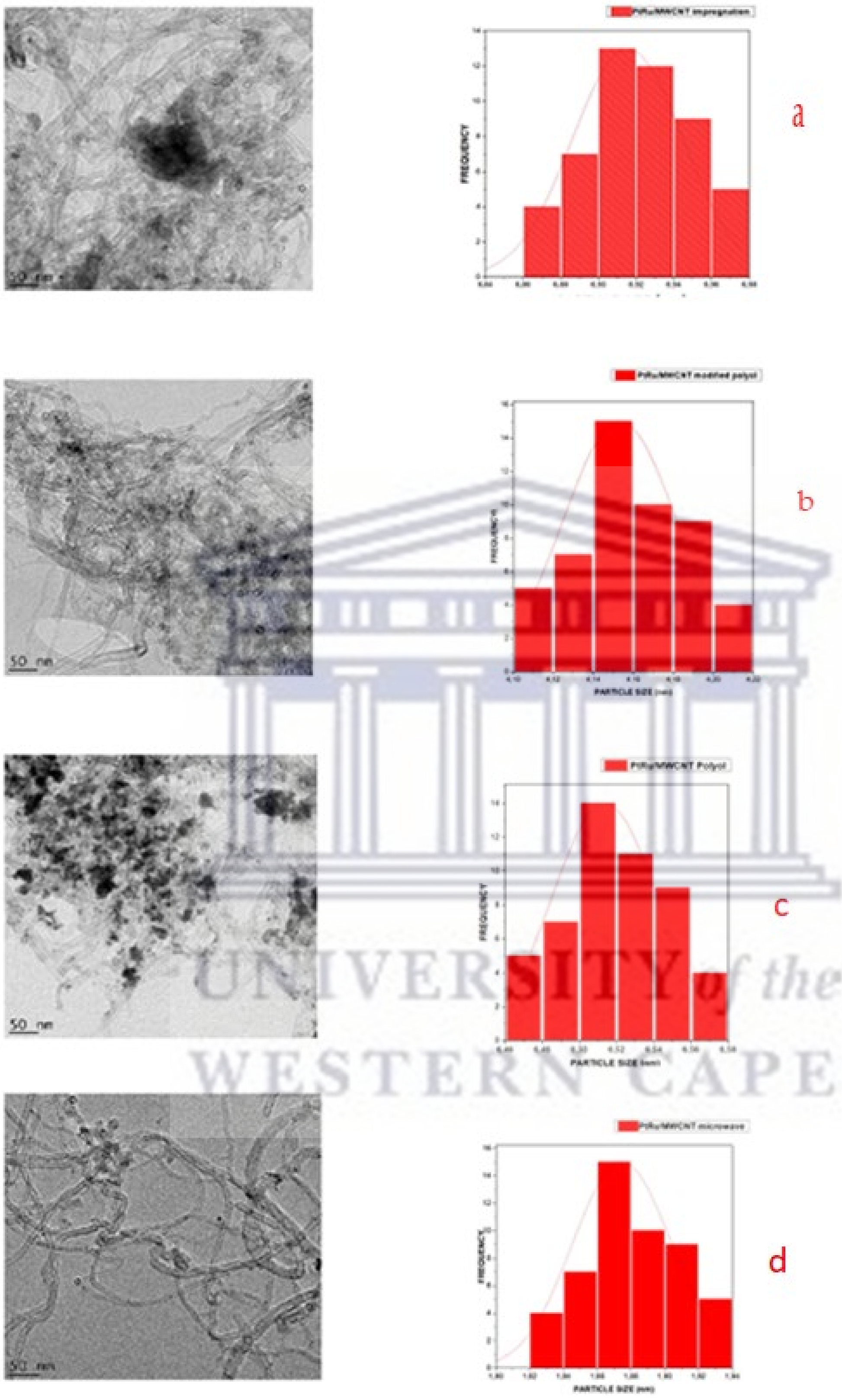

Figure 4. 2: HRTEM images with their respective histograms for PtRu/MWCNT electrocatalysts prepared through the impregnation, polyol, modified polyol and microwave assisted modified polyol methods.

Catalyst nanoparticles are the dark dots as shown in the HRTEM micrographs in Figure 4. 2

PtRu/MWCNT prepared through the impregnation method has more agglomeration. PtRu/MWCNT electrocatalysts prepared through the microwave-assisted modified polyol method has the least agglomeration, followed by PtRu/MWCNT modified polyol when compared with other electrocatalysts evident from their higher electroactive catalyst surface areas of 4.15 x 10^3 cm^2/g and 3.2 x 10^3 cm^2/g respectively an advantage for enhanced electrocatalytic activities. Both of these catalysts gave the smallest particle sizes of 1.87 nm and 4.14 nm, respectively. The particle size was determined using Image J software estimated from 50 particles selected randomly from HRTEM micrographs of the PtRu/MWCNT nanoparticles. The other electrocatalysts PtRu on MWCNT support particle sizes were between 5.77 nm and 6.90 nm. The particle sizes of the electrocatalysts obtained were comparable with the average particle sizes following the order PtRu/MWCNT impregnation > PtRu/MWCNT polyol > PtRu/MWCNT modified polyol > PtRu/MWCNT microwave-assisted modified polyol.

In Figure 4. 2 the histograms reveal the mean particle sizes and their nanoparticle size distributions for all PtRu/MWCNT electrocatalysts prepared through all four synthesis methods; however, the two electrocatalysts prepared through the microwave method and modified polyol method exhibited better distribution of nanoparticles as compared to other electrocatalysts. The mean particle sizes of PtRu/MWCNT impregnation, PtRu/MWCNT polyol, PtRu/MWCNT modified polyol and PtRu/MWCNT microwave-assisted modified polyol were 6.90 nm, 6.51 nm, 4.14 nm and 1.87 nm, respectively

4.1.3 Energy-dispersive X-ray spectroscopy (EDS) Analysis

Energy-dispersive X-ray spectroscopy (EDS) was utilized to determine the metal loading of the electrocatalysts. EDS results revealed binary catalyst PtRu/MWCNT prepared by the microwave assisted modified polyol method has a Pt wt.% of 21.37 comparable to binary catalyst PtRu/MWCNT prepared by polyol method of Pt wt % of 25.39 while PtRu/MWCNT catalyst prepared by modified polyol method of Pt wt % of 2.35% also comparable to PtRu/MWCNT prepared by impregnation method of Pt wt % of 2.05% . The composition of all the catalysts is given in Table 4. 2 All catalysts present atomic ratios that are comparable;

the information about the microstructure of the prepared electrocatalysts was determined using HR-TEM and XRD.

Table 4. 2: Atomic Compositions of Pt-Ru Catalysts; Nominal weight percentages obtained using energy-dispersive X-ray spectroscopy (EDS)

PtRu Catalysts	Precursor Pt:Ru	Actual Pt:Ru	Composition (%)	Metal loading (Pt) (W%)	Metal loading (Ru) (W%)
PtRu/MWCNT ModPoly	1:2	0.7: 0.34	32.7: 67.3	2.35	5.80
PtRu/MWCNT Polyol	1:2	2.17: 0.77	73.8:26.2	25.39	4.68
PtRu/MWCNT Impregnation	1:2	0.14: 0.96	12.7:87.3	2.05	7.42
PtRu/MWCNT Microwave	1:2	1.8: 1.28	58.4 41.6	21.37	7.86

4.2 Electrochemical characterisation of the electrocatalysts

Electrochemical measurements were carried out at ambient temperatures using a three-electrode configuration, which includes a working electrode, a counter electrode, and a reference electrode. An Ag/AgCl electrode as a reference electrode and a Pt foil of a large area as a counter electrode were used. The working electrode was a glassy carbon disc (5 mm in diameter with a geometric area of 0.196 cm^2) covered with a thin layer of catalyst of fine film. Before the experiment, the electrode substrate was pre-treated by polishing it with a 0.05µm Al_2O_3 particle suspension on a moistened microcloth. All the electrochemical experiments were carried out, namely electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and cyclic voltammetry (CV), and performed on an autolab electrochemical workstation (PGSTAT128N, Eco Chemie, the Netherlands). CA tests were carried out for the electrocatalytic stability of the PtRu/MWCNT catalysts for the methanol electro-oxidation. The CA was carried out for 30 minutes. CV evaluations were carried out at 30 mV/s covering a potential window from -0. 2 V to 1.2 V vs. Ag/AgCl. Perchloric acid was used as the electrolyte. Inert nitrogen gas was used to deaerate the solutions. To obtain a homogeneous catalyst layer, a stock solution was first prepared by mixing 20 ml of isopropanol, 79.6 ml of ultra-pure water and 0.4 ml of 5wt% Nafion solution in a 100-ml volumetric flask. Thereafter, 10 mg of the catalyst powder was measured into a 10-ml vial and 5 ml of stock solution was added, mixed thoroughly, and sonicated for 60 minutes in an ultrasonicator. A measured volume of this mixture was dropped on top of the glassy carbon disc and then dried to form the desired catalyst layer.

Electrochemical activities of the prepared catalysts in a 0.5 M $HClO_4$ solution were firstly examined by CV. From the CV of the prepared electrocatalysts, the adsorption peaks for the different catalysts were observed. The peak area of the adsorption peak of the electrocatalysts in the CV was used to determine the electroactive surface area of the catalysts using the equation 1.0 [24]

$$ECSA = \frac{Q}{210\mu C/cm2.m.Ag} \qquad 1.0$$

where Q is the charge from the Hydrogen adsorption peak in Coulomb taking within negative potential region of

-0.2 V to 0.08 V in the forward scan, as shown in Figure 4. 3, m is the working electrode Pt loading in mg cm^{-2}, Ag is the geometric surface area of the electrode (5 mm in diameter, Ag = 0.196 cm^2) and 210 µCcm^{-2} is the value for the charge of full coverage for a clean polycrystalline Pt monolayer [25].

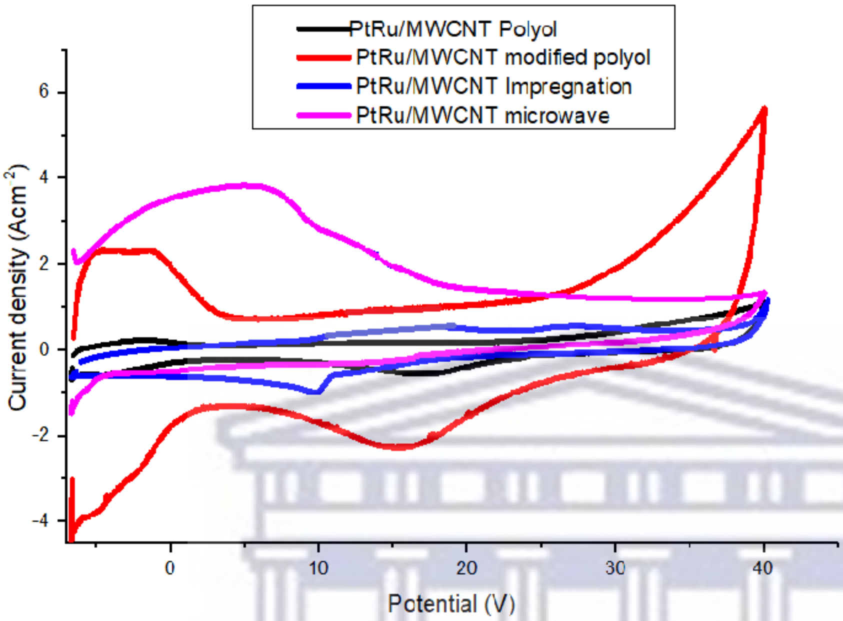

Figure 4. 3**:** Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N_2-saturated 0.5 M perchloric acid $HClO_4$ at a scan rate of 30mV.s^{-1}

The obtained ECSA values were 4.15 x 10^3 cm^2/g for PtRu/MWCNT microwave-assisted modified polyol, 3.2 x 10^3 cm^2/g for PtRu/MWCNT modified polyol, 0.35 x 10^3 cm^2/g for PtRu/MWCNT polyol and 0.28 x 10^{2}m^2/g for PtRu/MWCNT impregnation. The higher ECSA value of PtRu/MWCNT prepared through the microwave-assisted modified polyol method can be attributed to its lower particle size value, hence a higher surface area compared to the other electrocatalysts.

4.2.1 Methanol oxidation reaction

The electrocatalytic activity of the PtRu/MWCNT series catalysts towards the methanol oxidation was investigated using the CV technique in 0.5 M $HClO_4$ with 2 M methanol at a scan rate of 30 mVs^{-1}, as shown in Figure 4. 4

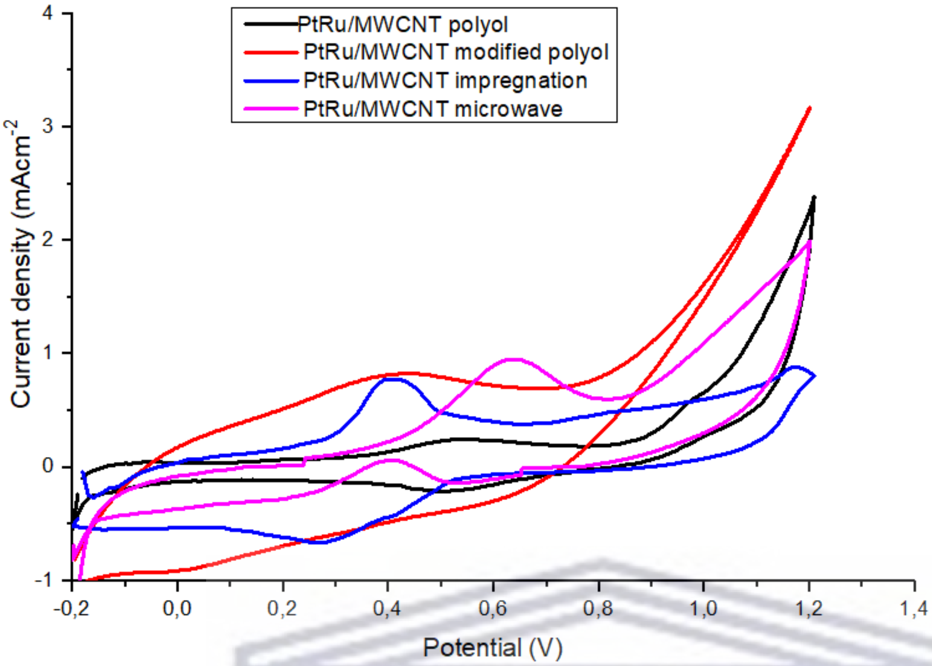

Figure 4. 4**:** Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N_2-saturated 0.5 M perchloric acid $HClO_4$ and 2 M methanol at a scan rate of 30mV.s^{-1}

The electrocatalytic activity towards methanol oxidation is summarised in Table 4. 3 By comparing the characteristics of the CVs, the change in catalyst preparation methods leading to varying compositions of Pt and Ru in the metal alloys was found to substantially enhance the catalytic activity for methanol electro-oxidation. First, the onset potentials (measure of catalytic activity) of methanol oxidation for the PtRu/MWCNT prepared through the microwave-assisted modified polyol method and PtRu/MWCNT showed relatively lower values than that of PtRu/MWCNT electrocatalysts prepared through the impregnation, polyol and modified polyol methods. The positions of the onset potentials follow the order of PtRu/MWCNT microwave-assisted modified polyol < PtRu/MWCNT modified polyol < PtRu/MWCNT polyol < PtRu/MWCNT impregnation. Second, the forward peak current densities (measure of the maximum catalyst performance) of the PtRu/MWCNT catalysts took the order PtRu/MWCNT microwave-assisted modified polyol > PtRu/MWCNT impregnation > PtRu/MWCNT modified polyol > PtRu/MWCNT polyol. Therefore, PtRu/MWCNT prepared through the microwave-assisted modified polyol method exhibited the most prominent electrochemical performance in terms of the highest forward peak current density and the lowest onset potential, followed by PtRu/MWCNT prepared through the modified polyol method.

Table 4. 3: Comparison of the electrocatalytic activity of the catalysts for methanol oxidation

PtRu electrocatalysts	$E_{(onset)\ [a]}$ [V vs. Ag/AgCl]	$E_{f\ [b]}$ [V vs. Ag/AgCl]	Ij [c] ($mAcm^{-2}$)	Electroactive catalyst surface area (cm^2/g)
PtRu/MWCNT modified polyol	-0.194	0.415	0.16	3.2×10^3
PtRu/MWCNT polyol	-0.187	0.522	0.041	0.35×10^3
PtRu/MWCNT impregnation	-0.151	0.411	0.188	0.28×10^3
PtRu/MWCNT microwave	-0.198	0.633	0.190	4.15×10^3

[a] Onset potential, [b] forward anodic peak potential at 30 mVs^{-1}, [c] forward anodic peak current density at 30 m Vs^{-1}

It was found that PtRu/MWCNT produced through the microwave-assisted modified polyol method of Pt : Ru ratio close to 1 : 1 outperformed all other PtRu/MWCNT electrocatalysts produced through other synthesis methods in methanol electro-oxidation reaction evident from the current density of 0.190 mA/cm^2.

Electro-oxidation of methanol to form CO_2 can be via dual path mechanisms consisting of non-CO and adsorbed CO reactive intermediates [26]:

$Pt(CH_3OH)ads + H_2O \longrightarrow CO_2 + 6H+ + 6e$

$Pt(CH_3OH)ads \longrightarrow Pt(CO)ads + 4H+ + 4e$

The non-CO reaction pathway is preferred for methanol oxidation for which it does not involve CO, a poison for Pt metal. The adsorbed CO reaction pathway often presents, however, in which the intermediates via (CO)ads are mostly in the form of linearly bonded CO, i.e. Pt = C = O [27]. Interaction of this complex on the catalyst surface leads to CO poisoning. The presence of Ru in the bimetallic catalyst assists in the oxidation of CO through chemisorbed -OH on the Ru sites [28]:

$\text{Ru} + \text{H}_2\text{O} \longrightarrow \text{Ru-OH} + \text{H}^+ + \text{e}^-$

$\text{Ru-OH} + \text{Pt(CO)ads} \longrightarrow \text{Ru} + \text{Pt} + \text{CO}_2 + \text{H+} + \text{e}^-$

In this way, the poisoned Pt is regenerated and can again participate in the oxidation of methanol. Due to the single species of CO and OH on Pt and Ru, respectively, the best results can be obtained when the Pt to Ru atomic ratio is 1 : 1 [29].

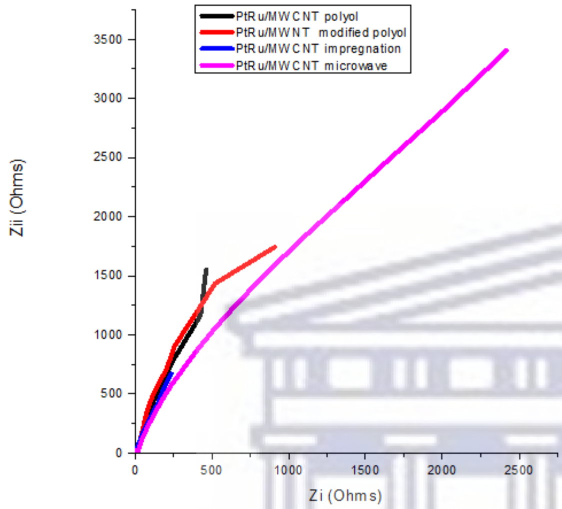

Figure 4. 5: Electrochemical impedance curves of methanol oxidation on PtRu/MWCNT electrocatalysts prepared through different synthesis methods in N_2-saturated 0.5 M HClO4 and 2 M methanol.

The EIS technique was used to investigate the catalytic reaction kinetics for the methanol oxidation on the anodic PtRu/MWCNT electrocatalysts surfaces. The charge transfer resistance (Rct) values using equivalent circuit fitting were 5.985 kΩ, 8.926 kΩ, 4.061 kΩ and 6.184 kΩ for PtRu/MWCNT modified polyol, PtRu/MWCNT polyol, PtRu/MWCNT impregnation and PtRu/MWCNT microwave-assisted modified polyol, respectively, indicating that PtRu/MWCNT prepared through the impregnation method exhibited the best kinetics towards the methanol electro-oxidation with the least resistance to flow of electric current. PtRu/MWCNT prepared through the modified polyol method also showed promising kinetics with an Rct value of 5.985 kΩ.

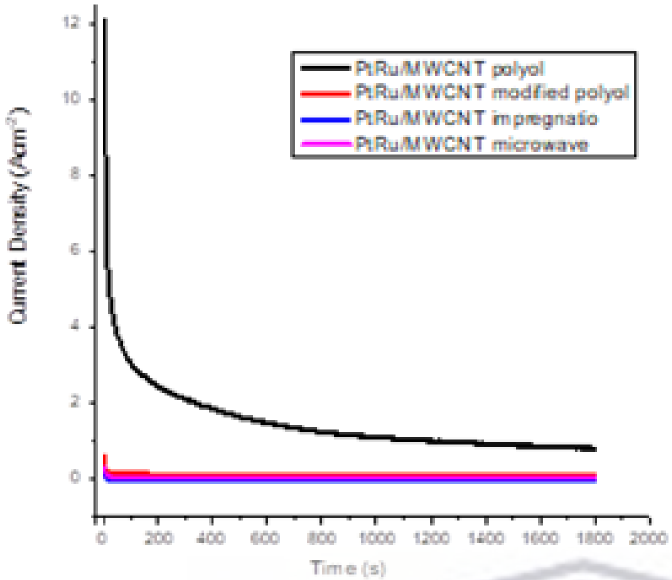

Figure 4. 6**:** Chronoamperometry curves of methanol oxidation on PtRu/MWCNT electrocatalysts in 0.5 M $HClO_4$ and 2.0 M CH_3OH

The stability of the electrocatalysts is extremely important for their real applications in direct methanol fuel cells. Figure 4. 6 shows the CA of PtRu electrocatalysts on MWCNT support in N_2-saturated 0.5 M $HClO_4$ with 2.0 M methanol. This was to test the stability of the different catalysts after 1 800 seconds. As observed at the start of the CA curve, the current density decreases sharply with time (I proportional to $t^{-1/2}$). The decreasing rate with time may characterise the inhibition of the electrodes by the methanol oxidation reaction products. When comparing the prepared catalysts, PtRu/MWCNT catalyst prepared through the polyol method performed better, followed by PtRu/MWCNT modified polyol. PtRu/MWCNT prepared by microwaving also showed a better stability with higher current density than PtRu/MWCNT prepared through the impregnation method.

4.3. CONCLUSION

In this study, PtRu, supported on MWCNT, was successfully fabricated using the impregnation, polyol, modified polyol and microwave-assisted modified polyol catalyst preparation methods. The synthesised electrocatalysts had crystalline sizes of 1.95–7.11 nm and average particle sizes of 1.87 – 6.90 nm, determined using XRD and HRTEM, respectively. The PtRu alloy phase is pronounced for the prepared electrocatalysts according to XRD analysis. It is found that the PtRu/MWCNT electrocatalyst produced through the microwave-assisted modified polyol method and PtRu/MWCNT modified polyol showed enhanced electrocatalytic activity towards methanol oxidation compared to other PtRu electrocatalysts on MWCNT support. Furthermore, the microwave-assisted prepared PtRu/MWCNT electrocatalyst had the largest current density for methanol oxidation compared to other electrocatalysts. This can be attributed to it having the smallest particle size and being the most active toward anode oxidation reaction. From the EIS, it was concluded that the PtRu/MWCNT electrocatalysts produced through the impregnation method exhibited a faster electrochemical reaction kinetics than both PtRu/MWCNT electrocatalysts produced through the polyol and modified polyol methods. Microwave-assisted modified polyol method PtRu electrocatalysts had the highest ECSA values compared to all other PtRu catalysts on MWCNT support, followed by PtRu/MWCNT produced by modified polyol method. This was a result of their smaller crystalline particle sizes of 1.95 nm and 4.33 nm, respectively. Polyol method synthesised PtRu/MWCNT was found to be the most stable electrocatalyst, followed by PtRu/MWCNT produced through the modified polyol method, as revealed by the Chronoamperometry tests.

Based on all the results acquired in this investigation, it was concluded that the microwave-assisted modified polyol process of catalyst preparation method produced the best PtRu electrocatalyst on MWCNT support of improved catalytic activity.

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CHAPTER 5

RESULTS AND DISCUSSIONS ON TERNARY CATALYSTS SYNTHESIZED BY MICROWAVE ASSISTED MODIFIED POLYOL METHOD

ABSTRACT

This study investigates the best electrocatalyst for methanol oxidation reaction (MOR) for four synthesized electrocatalysts, PtRu, PtRuIr, PtRuW and PtRuMo prepared by microwave assisted modified polyol method and PtRu/C commercial catalyst in acidic medium. All the synthesized Platinum based binary and ternary metal alloys were supported on the functionalized multi-walled carbon nanotubes (MWCNT). High resolution transmission electron microscopy, HR-TEM and Xray diffraction analysis, XRD techniques were used to determine the particle size and crystalline size of the electrocatalysts, respectively while Energy dispersive analysis Spectroscopy, EDS was used to determine elemental compositions. XRD crystalline sizes were from 1.36 nm to 4.96 nm while for HR-TEM particle sizes are in the range of 1.20 nm and 5.33 nm. The electroactivity and electroactive surface area, reaction kinetics and stability of the electroccatalysts towards methanol oxidation were evaluated using cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperomery respectively. The ternary catalyst PtRuMo/MWCNT was the most electrochemically active showing highest electrocatalytic mass activity of 51.8A/g. PtRuIr/MWCNT electrocatalyst performed better than the commercial catalyst PtRu/C with mass activities of 22.68A/g and 16.34A/g respectively.

5.0 Introduction

There is a need for alternative materials for electrocatalysts because noble metal resources are rare and the platinum and ruthenium utilized with the precursors for electrode catalyst are highly expensive. The use of a modified catalyst is essential to minimize the noble metal loading and optimizing catalytic efficiency.

To enhance the efficiency of the electrocatalyst for the electro-oxidation of methanol, numerous researchers have thoroughly worked on Pt-based binary, ternary, and even quaternary compounds [1–4]. However, there are still certain challenges in the development of Pt-based catalysts, such as support material development, research and development of non-noble metal catalysts, high-index crystal synthesis, and high-precision control of particle size

[5]. In carrying out this research we believe that the use of fuel cells in new energy systems has a promising future owing to continuing technological and material characterisation improvements along with ongoing theoretical research, which is focused on the study of Pt-based catalyst modification.

Catalyst preparation methods have an influence on the mean particle size, particle size distribution, the bulk and surface of catalysts composition, the oxidation state of catalysts, the extent of catalyst alloying, the distribution of catalyst crystal surfaces, the catalyst morphology, [6,7], hence on the catalytic activity of the metal catalysts [8]. The standard by which high performance catalysts are evaluated includes a uniform composition in the entire nanoparticles, a complete alloyed degree, a narrow nanoscale size distribution and high dispersion on carbon support [9]. All these methods include a chemical step for developing nanoparticles and a deposit step for dispersing the electrocatalyst onto the carbon particles.

Direct alcohol fuel cells (DAFC) are excellent sources of energy because of their low pollutant emission, high energy density like 6.13kWh/Kg for direct methanol fuel cells, DMFCs, low operating temperature and the ease of handling a liquid fuel [10-13]. The DMFC which is a low temperature fuel cell has attracted considerable attention for portable power applications and possess several advantages. The use of methanol as the liquid fuel is essential for commercial use because it can be easily transported and stored, less safety concern, and relatively small investment needed for placing the relevant support infrastructure. Another advantage is that these fuel cells can achieve efficiencies of up to 40%.

DMFCs are available at very high cost because of the electrocatalysts mostly used which is platinum based which is very expensive. This can be overcome by using reduced amounts of the catalyst without reducing the efficiency of the cell or non – platinum-based catalysts or synthesizing binary/ternary alloy of the metal for a by-functional or electronic effects. Hence the focus of this study is synthesizing ternary catalysts PtRuIr/MWCT, PtRuMo/MWCNT and PtRuW/MWCNT and comparing with binary catalyst PtRu/MWCNT using the microwave assisted modified polyol method reported as the best catalytic preparation method for enhanced catalytic electroactivity [14].

Platinum/Ruthenium alloys are the most practical electro-catalysts for the DMFC application for exhibiting enhanced electroactivity and stability. For a single noble metal platinum electrocatalyst, the adsorption of CO, one of the intermediates in methanol electro-oxidation, can inhibit the reaction active sites, resulting in slow reaction kinetics. Using a second metal, such as ruthenium, alloying with platinum the oxidation kinetics of methanol are increased significantly. The mechanism of methanol oxidation on the Platinum surface has been investigated extensively for decades. According to a detailed mechanism [15], the primary processes of methanol oxidation on the platinum surface include the following steps such as: (1) CH_3OH adsorption; (2) CH_3OH dissociation (C–H bond activation); (3) H_2O adsorption; (4) H_2O activation; (5) oxidation of CO. The formation of OH by H_2O activation on the platinum surface, requires a high potential, this step is necessary for the oxidative removal of adsorbed CO. The mechanism of methanol oxidation on the Platinum surface is shown below [16];

Pt + CH_3OH → Pt─CH_2OH + H^+ + e- [1]
Pt + CH_2OH → Pt─CHOH + H^+ + e- [2]
Pt + CHOH → Pt─COH + H^+ + e- [3]
Pt + COH → Pt─CO + H^+ + e- [4]
Pt + H2O → Pt─OH + H^+ + e- [5]
Pt ─CO + Pt─OH → 2Pt + CO_2 + H^+ + e- [6]

The reactions (1-4) represent the methanol electrosorption processes which involve CH_3OH adsorption; and CH_3OH dissociation (C–H bond activation while (5-6) are the representation of the oxygen removal or oxidation of intermediates.

For anodic methanol oxidation, such a high potential gives a limitation to the fuel cell application of a pure platinum catalyst. In order to improve the catalytic performance and to decrease the poisoning effect of anode catalysts, many investigations have been conducted on the development of Pt-based binary catalysts, such as bimetallic Pt-based alloys, such as PtRu [17-23], PtW [24,25], PtMo[26] PtSn[26-28] and PtOs[29,30]. So far, the Pt–Ru alloy has been found to be the most active bimetallic catalyst and is the state-of-the-art anode catalyst for DMFCs.

We report herein an electrochemical investigation of the microwave assisted modified polyol synthesized PtRu/MWCNT, PtRuIr/MWCNT, PtRuMo/MWCNT, PtRuW/MWCNT and PtRu/C commercial catalysts used for anodic methanol oxidation in acidic electrolyte. Characterizations were done by using various physicochemical analyses such as high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and Energy dispersive analysis Spectroscopy, (EDS). The electrocatalytic activities of the electrocatalysts were investigated using the cyclic voltammetry (CV), chronoamperometry (CA) and the electrochemical impedance spectroscopic, (EIS) methods.

5.1. Results and discussion

5.1.1. Physical characterization of the prepared electrocatalysts

To have more information on the catalyst structure, X-ray diffraction (XRD) patterns were performed using Bruker AXS D8 Advance instrument, Cu-K_α radiation, λ = 1.5406 Å. The Bragg angle range was 2θ = 10–90° with a scanning step of 0.035°. A standard α-Al_2O_3 sample was used for the determination of the instrumental contribution into peak profile parameters.
The high-resolution transmission electron microscope (HR-TEM) micrographs were obtained using a JEOL 2010 TEM system operating at 200 kV. The HR-TEM samples were prepared by dispersing the carbon-supported electrocatalysts in ethanol, and then a drop of the suspension was cast onto the carbon film covered Cu-grid for analysis. The particle size determined by HR-TEM was obtained using Image J software (Image Processing and Analysis in Java developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation LOCI, University of Wisconsin, Madison, WI, USA) over multiple areas for each electrocatalyst. Energy dispersive X-ray spectroscopy (EDS) coupled to the scanning electron microscopy (JOEL JSM-7500F Scanning Electron Microscope, Mundelein, IL, USA), evaluated the catalyst composition.

5.1.1.1. Energy-dispersive X-ray spectroscopy (EDS) Analysis

Energy-dispersive X-ray spectroscopy (EDS) was utilized to determine the metal loading of the electrocatalysts. Binary catalyst PtRu/MWCNT prepared by the microwave assisted modified polyol method has a Pt wt.% of 21.37 comparable to ternary catalyst PtRuMo/MWCNT of Pt wt % of 21.64 and PtRu/C commercial catalyst of Pt wt % of 20%. These three catalysts are composed of Ru wt% of 7.86%, 7.35% and 10% respectively. Ternary catalysts PtRuIr /MWCNT has the least Pt content of 6.44%. The composition of all the catalysts is given in Table 1. All catalysts present atomic ratios that are comparable; the information about the microstructure of the prepared electrocatalysts was determined using HR-TEM and XRD.

Table 5. 1: Atomic Compositions of PtRu/MWCNT and PtRu(X)/MWCNT Catalysts; Nominal weight percentages obtained using energy-dispersive X-ray spectroscopy (EDS)

PtRu Catalysts	Precursor Pt:Ru:X	Actual Pt:Ru;X	Composition (%)	Metal loading (Pt) (W%)	Metal loading (Ru) (W%)	Metal loading (X=Ir, Mo, W) (W%)
PtRu/MWCNT	1:2	1.8: 1.28	58.4: 41.6	21.37	7.86	-
PtRu/C	1:2	1.33: 0.86	60.7:39.3	17.10	5.75	-
PtRuIr/MWCNT	1:2:2	0.62: 2.32:1.91	12.7:47.8:39.5	6.44	12.57	19.71
PtRuMo/MWCNT	1:2:2	1.89: 1.24:0.55	51.4:33.7:14.9	21.64	7.35	3.12
PtRuW/MWCNT	1:2:2	1.25:0.85:0.07	57.6:39.17:15.19	16.05	5.64	0.82

From Table 5. 2 below the average particle size can be seen, with PtRuMo/MWCNT nanoparticles having the smallest crystalline size of 1.36 nm, followed by PtRuIr/MWCNT nanoparticles with a crystalline size of 4.33 nm .As evident from the table, PtRuMo/MWCNT has the highest electcroactive catalyst surface area of 180m^2/g as compared to other electrocatalysts.

Table 5. 2: Properties of the PtRu/MWCNT and PtRu(X)/MWCNT Catalysts; Crystallite sizes of the electrocatalysts were calculated using Scherrer's equation and particle sizes obtained using high-resolution transmission electron microscopy (HR-TEM).

Electrocatalysts	Crystalline size(nm)	Particle size(nm)	Electroactive catalyst surface area (m^2/g)
PtRu/MWCNT	1.95	1.87	129.7
PtRuIr/MWCNT polyol	1.70	1.65	77
PtRuMo/MWCNT impregnation	1.36	1.20	180
PtRuW/MWCNT microwave	4.96	5.33	4.12
PtRu/C commercial	2.25	2.11	82.1

ECSA=Electroactive Catalyst Surface Area.

5.1.1.2. XRD Analysis

XRD measurements were made to determine the crystalline details of the produced catalysts. According to the X-ray diffraction (XRD) results shown in figure 5. 1, all of the metal catalysts that had been synthesized displayed the face-centered cubic (fcc) crystallographic structure that is typical of a pure platinum structure. The Bragg's angles show that various bimetallic and trimetallic interactions or alloying happened in the PtRu and PtRu(X) crystals because the electrocatalysts made using the microwave aided modified polyol technique had different elemental compositions. About $2\theta = 25^0$ is where the carbon diffraction peak is located. Other peaks are found at 2θ values of 39.9^0, 46.21^0, 67.8^0, and 81.2^0, which correspond to the (111), (200), (220), and (311) planes of the Pt crystal structure.

The strongest and sharpest diffraction peaks for two ternary catalysts PtRuIr and PtRuMo and the bimetallic PtRu samples are at around $2\theta = 39.9^0$ indexed as (111) reflection of PtRuIr/MWCNT, PtRuMo/MWCNT and PtRu/MWCNT crystal planes respectively. PtRuW showed its sharpest diffraction peak at 46.21^0 which is indexed as (200) reflection planes of PtRuW/MWCNT crystal structure. Other characteristic PtRu/ MWCNT and PtRu(X)/MWCNT diffraction peaks at 2θ of about 46.21^0, 67.8^0 and 81.2^0 corresponded to (200), (220) and (311), respectively. A similar results were also reported by Youngmin Kim et al [31] and Bohua Wu et al [32] for PtRu/MWCNT crystals and Yanjiao et al [33]. Wang. Z.B et al [34] and Kang D.K et al [35] for PtRuIr/C, PtRuMo/C and PtRuW crystalline structures respectively.

The crystalline size of the metal particles is calculated using Debye- Scherrer's equation, $K\alpha/\beta\cos\theta$, Where K, Scherrer constant, $\alpha = 0.9$, X-Ray wavelength $= 0.154$nm. $\beta(2\theta)$, the width of the diffraction peak (rad). From table 2 the average particle size can be seen with PtRuMo/MWCNT nanoparticles prepared by the microwave assisted modified polyol having the least crystalline size of 1.36nm followed by PtRuIr/MWCNT nanoparticles of crystalline size of 1.70nm

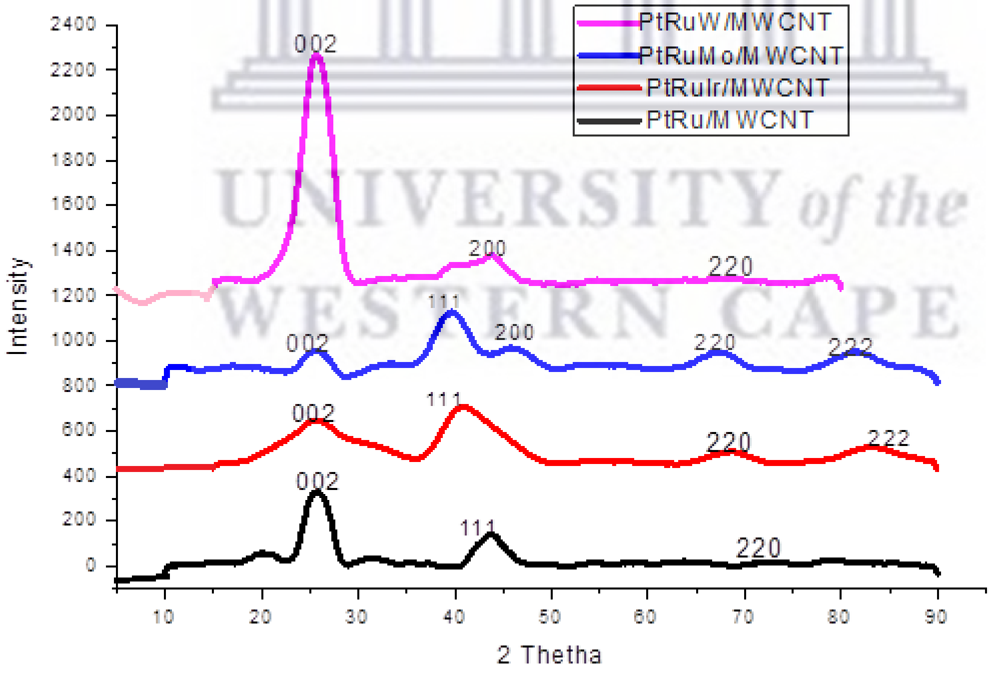

Figure 5. 1: XRD spectra of PtRu and PtRu(X) electrocatalysts supported on MWCNTs prepared by the microwave assisted modified polyol method.

The dark dots in the HRTEM micrographs in fig. 5. 1 above are catalyst nanoparticles. The nanoparticles of PtRu/MWCNT and PtRu(X)/MWCNT are evenly dispersed and rarely aggregated nanoparticles. As compared to other electrocatalysts, the PtRuMo/MWCNT electrocatalyst prepared by the microwave assisted modified polyol method exhibits the least agglomeration, followed by the bimetallic PtRu/MWCNT catalyst, which benefits from higher electroactive surface areas of 180 m^2/g and 129.7 m^2/g, respectively. With 1.20 nm particle diameters, PtRuMo/MWCNT catalysts had the smallest size. The particle sizes of the other electrocatalysts, which were PtRu-based and supported by MWCNT, ranged from 1.60 nm to 5.35 nm. The particle sizes were calculated using 50 nanoparticles of the electrocatalysts using image j software. The particle sizes in the following order: PtRuW/MWCNT > PtRu/MWCNT > PtRuIr/MWCNT > PtRu/C > PtRuMo/MWCNT. The histogram in fig.5 1 also revealed the well distribution of all the nanoparticles prepared by the microwave assisted modified polyol method. The mean particles sizes of PtRu/MWCNT, PtRuIr/MWCNT, PtRuMo/MWCNT and PtRuW/MWCNT and PtRu/C commercial catalysts are 1.87nm, 1.65nm, 1.20nm and 5.33nm and 2.11nm respectively.

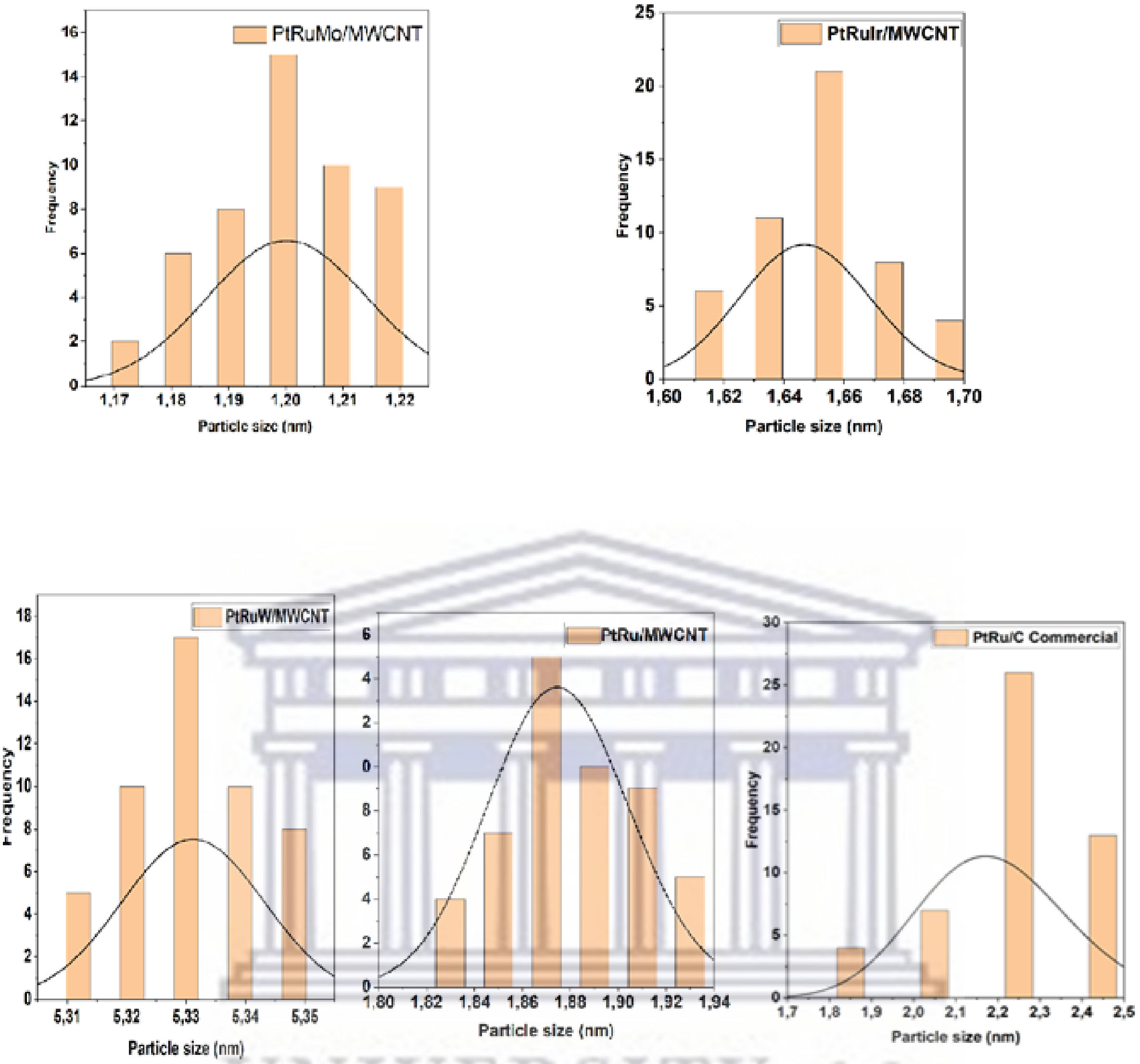

Figure 5. 2**:** Histograms showing nanoparticles mean particles sizes and distributions.

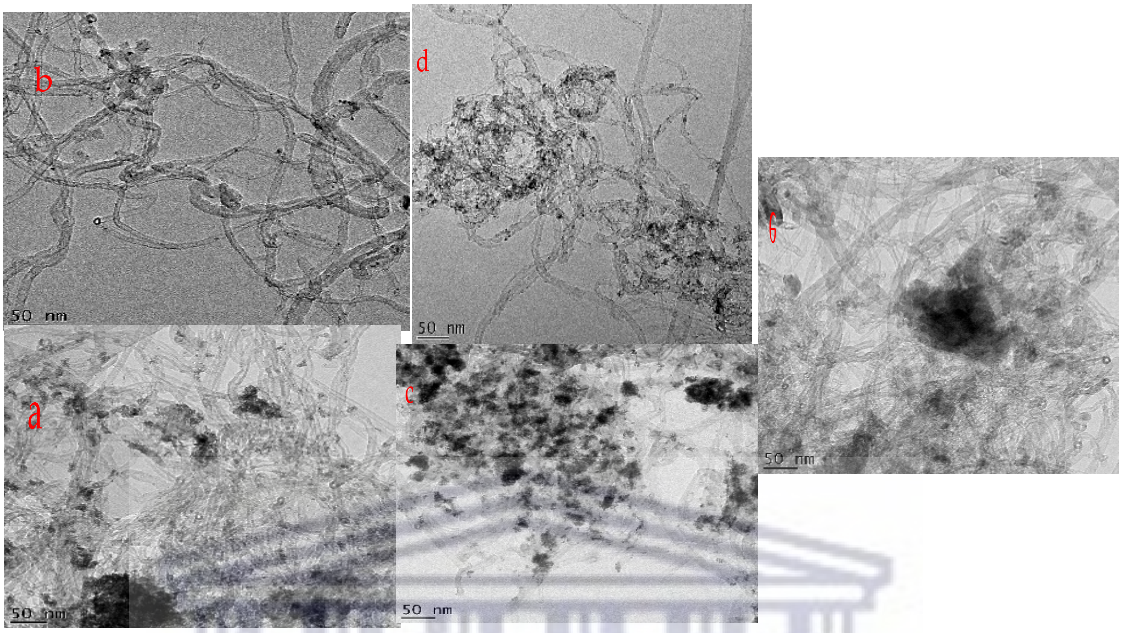

Figure 5. 3: HR-TEM micrographs of (a) PtRu/C (b)PtRu/MWCNT (c) PtRuIr/MWCNT and (d)PtRuW/MWCNT and (e) PtRuMo/MWCNT

5.2 ELECTROCHEMICAL CHARACTERIZATION OF THE ELECTROCATALYSTS

Electrochemical measurements were carried out at ambient temperatures using a three-electrode configuration, which includes each of working electrode, counter electrode, and reference electrode. An Ag/AgCl electrode as a reference electrode and a Pt foil of large area as a counter electrode were used. The working electrode was a glassy carbon disc (5 mm in diameter with a geometric area of 0.196 cm^2) covered with a thin layer of catalyst of fine film. Before the experiment, the electrode substrate was pre-treated by polishing with a 0.05µm Al_2O_3 particle suspension on a moistened microcloth. All the electrochemical experiments were carried out namely electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and cyclic voltammetry (CV) and performed on an autolab electrochemical workstation (PGSTAT128N, Eco Chemie, Netherlands).

The stability of the PtRu/MWCNT catalysts for the methanol electrooxidation was tested using chronoamperometry for a period of 30 minutes. The potential window for the CV measurements, which ranged from -0.2 V to 1.2 V against Ag/AgCl, was covered at 30 mV/s. The electrolyte utilized was 0.5M perchloric acid. The solutions were deaerated for 1 hour using inert nitrogen gas. A stock solution was first made by combining 20ml of isopropanol, 79.4ml of ultra-pure water, and 0.4ml of a 5wt% Nafion solution in a 100ml volumetric flask.

This allowed for the creation of a homogeneous catalyst layer. A 10ml vial containing 10mg of the catalyst powder and 5ml of the stock solution was then filled, fully mixed, and ultrasonically processed for 60 minutes. The glassy carbon disc was covered with a measured amount of this mixture, which was then dried to make the needed catalyst layer.

Cyclic voltammetry was used to initially assess the electrochemical activity of the produced catalysts in a 0.5M HClO4 solution. The adsorption peaks for the various catalysts could be seen from the cyclic voltammetry of the electrocatalysts that had been synthesized. Equation (1) was used to calculate the electro-active surface area of the catalysts using the peak area of the adsorption peak of the electrocatalysts in cyclic voltammetry [36]

$$ECSA = \frac{Q}{210\mu C/cm2.m.Ag} \tag{1}$$

Ag is the geometric surface area of the electrode (5 mm in diameter), Q is the charge from the adsorption peak of in Coulomb taking within in negative potential region -0.2 V to 0.08 V in the forward scan, and 210 µ Ccm^{-2} is the value for the charge of full coverage for clean polycrystalline Pt monolayer [37].

The obtained ECSA values are 180m^2/g for PtRuMo/MWCNT, 77m^2/g for PtRuIr/MWCNT, 41.2 m^2/g for PtRuW/MWCNT, 129.7 m^2/g for PtRu/MWCNT and 82.1 for PtRu/C. Higher ECSA value of 180 m^2/g for PtRuMo/MWCNT when compared to other electrocatalysts can be attributed to its smallest particle size value of 1.20nm.

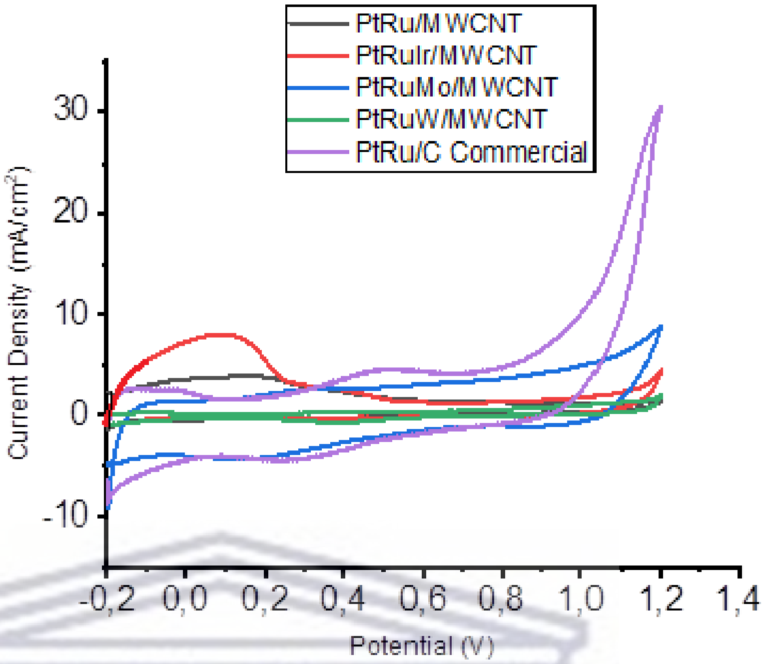

Figure 5. 4**:** Cyclic voltammograms of PtRu/MWCNT and PtRu(X)/MWCNT electrocatalysts in N_2 saturated 0.5 M Perchloric acid, $HClO_4$ at a scan rate of $30mVs^{-1}$.

5.2.1 Methanol oxidation reaction

The electrocatalytic activity towards methanol oxidation are summarized in Table 5. 4. By comparing the characteristics of the CVs, the varying elemental components of different compositions of Pt, Ru and Ir or Mo or W in the metal alloys was found to substantially enhance the catalytic activity for methanol electrooxidation. First, the onset potentials (measure of catalytic activity) of methanol oxidation for the ternary catalysts PtRuMo/MWCNT showed relatively lower values than that of other electrocatalysts. The positions of the onset potentials follow the order of PtRu/MWCNT < PtRuMo/MWCNT < PtRuW/MWCNT < PtRu/C< PtRuIr/MWCNT. Second, the forward peak current densities (measure of the maximum catalyst performance) of the binary catalysts and ternary catalysts took the order PtRuMo/MWCNT >PtRuIr/MWCNT > PtRu/C commercial > PtRuW/MWCNT> PtRu/MWCNT. The superior methanol oxidation reaction catalytic mass activities of the prepared electrocatalysts were determined using their current densities and the catalyst mass loading. PtRuIr/MWCNT and PtRuMo/MWCNT of smaller particle sizes of 1.65nm and 1.20nm respectively and higher current densities have shown better electrocatalytic mass activities of 51.8A/g and 22.68A/g respectively. PtRu/C commercial catalyst is next to them with 16.34A/g in electrocatalytic mass activity. Ternary PtRuW/MWCNT and binary PtRu/MWCNT exhibited electrocatalytic mass activities of 5.69A/g and 1.86A/g respectively.

Table 5. 3: Comparison of the electrocatalytic activity of the catalysts for Methanol Oxidation.

PtRu Electrocatalysts	$E_{(onset)}$ [a] [V vs. Ag/AgCl]	Current density ($mAcm^{-2}$)	Catalytic Mass activity (A/g)
PtRu/MWCNT	-0.198	0.190	1.86
PtRuIr/MWCNT	-0.180	2.314	22.68
PtRuMo/MWCNT	-0.194	5.283	51.79
PtRuW/MWCNT	-0.191	0.580	5.69
PtRu/C Commercial	-0.187	1.667	16.34

$E_{(onset)}$ = onset potential

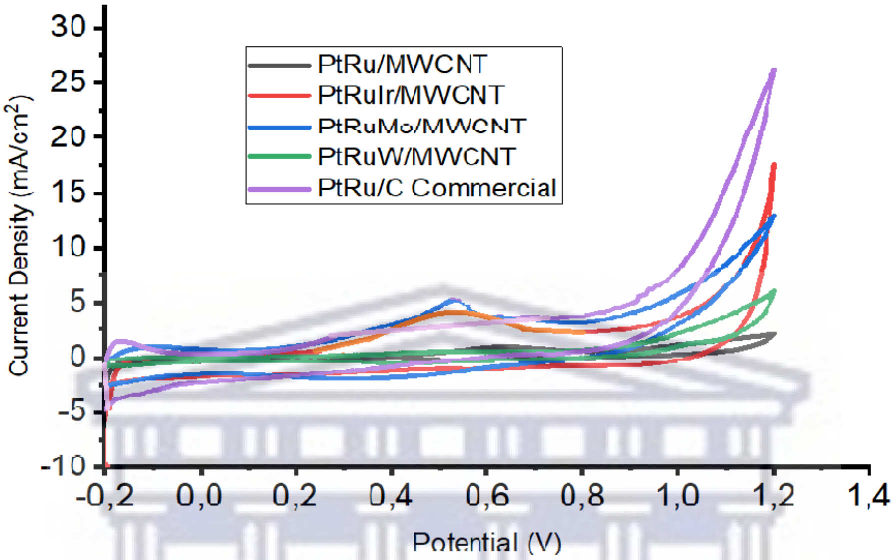

Figure 5. 5: Cyclic voltammograms of PtRu/MWCNT and PtRu(X)/MWCNT electrocatalysts in N_2 saturated 0.5 M Perchloric acid, $HClO_4$ and 2M Methanol at a scan rate of $30mVs^{-1}$.

5.3 Analysis of Mo,Ir and W influence on Methanol Electrooxidation

The enhanced performances of PtRuMo/MWCNT, PtRuIr/MWCNT and PtRuW/MWCNT ternary electrocatalysts, compared with that of PtRu/MWCNT, have hereby been ascribed to Mo, Ir and W additive, the effect of which can be explored from three aspects: the bifunctional mechanism, the hydrogen-spillover phenomena, and the modification of Pt electronic states. The bifunctional mechanism has been established in the previous studies as follows [38]:

$$MoOx + H_2O \rightarrow (MoOx)\text{-}OHads + H^+ + e^- \quad (2)$$

$$Pt\text{-}(CO)ads + (MoOx)\text{-}OHads \rightarrow CO_2 + H^+ + Pt + MoOx + e^- \text{ (Same for } IrO_x \text{ and } WO_x) \quad (3)$$

It can be seen that MoO*x* promotes the water activation, which generates the species of OHads to oxidize CO subsequently. This accounts for the enhanced activity of the PtRuMo/MWCNT, PtRuIr/MWCNT and PtRuW/MWCNT catalysts during the process of methanol electrooxidation. On the other hand, previous research on Pt-WO*x* nanophases indicated that hydrogen on the top site of Pt atom could migrate to the site over WO*x* at the positive potential in such a process that can be described with the following Eq. (4) [39,40,41]:

$$\text{Pt-H}_{\text{ads}} + \text{WO}x \rightarrow \text{Pt} + \text{H-WO}x \qquad (4)$$

which is the so-called “hydrogen spillover” from Pt to WO*x*. The transfer of hydrogen liberates the Pt active sites, which otherwise would have been blocked by hydrogen during the electrooxidation of methanol. A similar situation in PtRuMo/MWCNT nanoparticles can be imagined here, with the following proposed scheme of the hydrogen-spillover process [41]:

$$\text{MoO}x + \text{Pt-Hads} \rightarrow \text{H-MoO}x + \text{Pt} \qquad (5)$$

Such a process relieves the CO poisoning process caused by the adsorption of hydrogen. In addition, as the Mo oxides consist of mixed-valences, MoO*x* are relatively stable in acid solution and have relatively high electronic conductivities in the surface of the PtRuMo/MWCNT nanoparticles, owing to their TiO2-type structure with the short metal–metal distance along the shared edges [38,42].

The modification of electronic states for Platinum may subsequently change the catalytic activity of platinum in the Methanol electrooxidation process. In addition, the transfer of the electron density from Mo to Pt may occur, since the electronegativity of Mo is 2.16 while that of Pt is 2.28. The apparent effect is that the catalytically active sites are increased because the coverage of COads on the Pt surface is reduced due to the decreased Pt-CO binding energy caused by the electron density transfer. The electronegative values of W and Ir metals are 2.36 and 2.20 respectively this accounted for the higher catalytic performance of PtRuMo/MWCNT as compared to PtRuIr/MWCNT and PtRuW/MWCNT as PtRuMo/MWCNT has got more electron density around its platinum region as compared to the other two ternary electroacatalysts.

In summary, the improved performance of PtRuMo/MWCNT nanoparticles may be the combined effect of the bifunctional mechanism, the hydrogen-spillover effect, and the modification of the Pt electronic states. The enhanced activities of PtRuMo/MWCNT, PtRuIr/MWCNT and PtRuW/MWCNT ternary electrocatalysts are convincingly throwing some light on the research and development of effective DMFC catalysts.

Electrochemical impedance spectroscopy technique was used to investigate the catalytic reaction kinetics for the methanol oxidation on the anodic PtRu/MWCNT, PtRuW/MWCNT, PtRuIr/MWCNT, PtRuMo/MWCNT and PtRu/C electrocatalysts surfaces.

The charge transfer resistance, Rct values using equivalent circuit fitting were 1.045kΩ, 81.043kΩ, 7.300kΩ, 6.184kΩ and 1.99 kΩ for PtRuMo/MWCNT, PtRuIr/MWCNT, PtRuW/MWCNT, PtRu/MWCNT and PtRu/C respectively as shown in Table 5. 4 below indicating that PtRuMo/MWCNT with Rct value of 1.045kΩ exhibited best kinetics towards the methanol electrooxidation with the high conductivity to the flow of electric current followed by the PtRu/C commercial catalyst of Rct value of 1.99 kΩ.

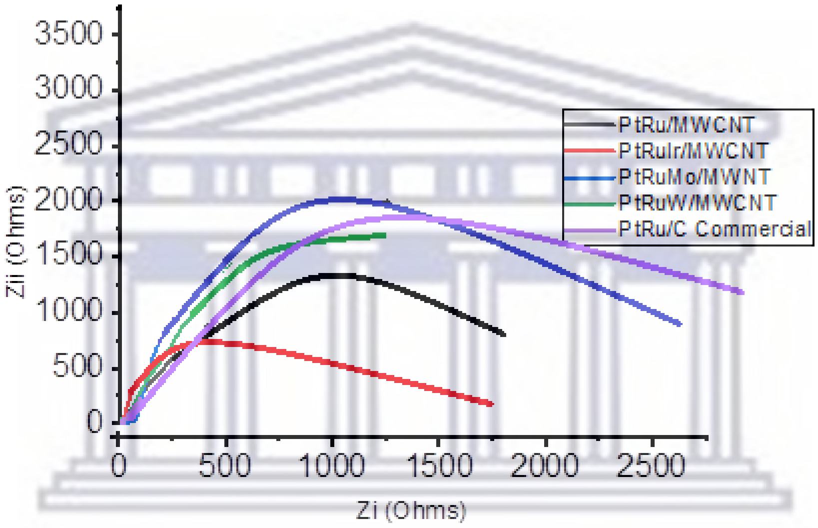

Figure 5. 6: Electochemical impedance curves of methanol oxidation on PtRu/MWCNT and PtRu(X)/MWCNT electrocatalysts in N_2 saturated 0.5M HClO4 and 0.2M Methanol.

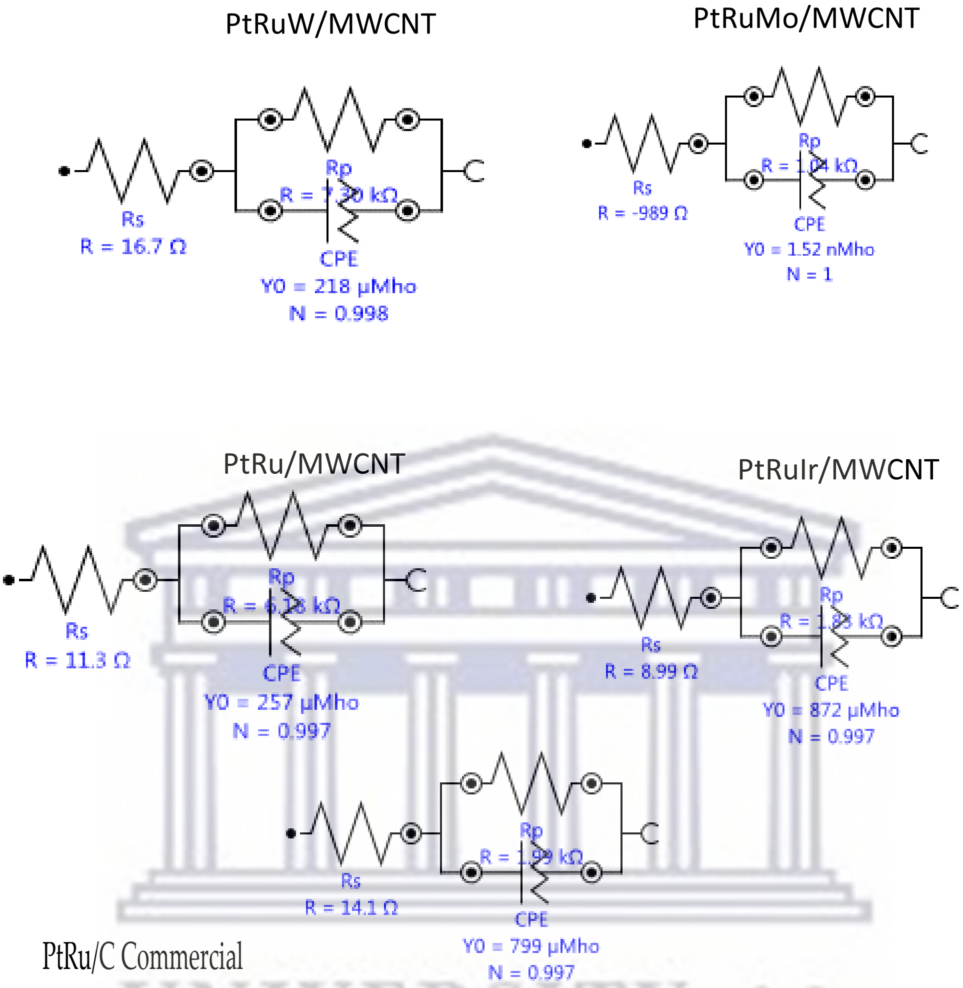

Figure 5. 7: Equivalent circuits for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT and PtRu(X)/MWCNT electrocatalysts in N_2 saturated 0.5M HClO4 and 0.2M Methanol.

Rp=Rct = Charge Transfer Resistance estimated from the equivalent circuit

Table 5. 4: Charge Transfer Resistance of PtRu/MWCNT and PtRu(X)/MWCNT electrocatalysts.

PtRu/MWCNT/ PtRu(X)/MWCNT	**Charge Transfer Resistance(kΩ)**
PtRu/MWCNT	6.184
PtRuIr/MWCNT	81.043
PtRuMo/MWCNT	1.045
PtRuW/MWCNT	7.300
PtRuC/C	1.99

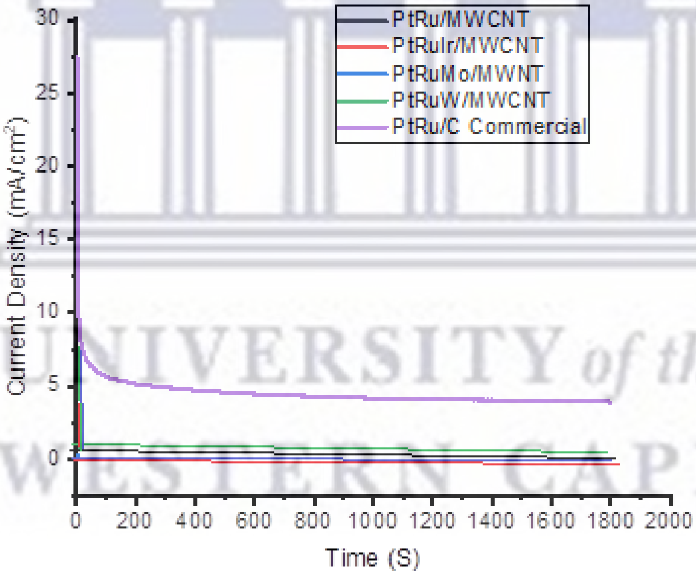

Figure 5.8: The Chronoamperometry Curves of methanol oxidation on PtRu/MWCNT. electrocatalysts in 0.5M $HClO_4$ and 2.0M CH_3OH.

For the electrocatalysts to be used effectively in DMFCs, stability is vital. In N_2 saturated 0.5M HClO4 with 2.0M methanol, Figure 5. 8 displays the chronoamperometry (CA) of PtRu electrocatalysts on MWCNT support. This was done to evaluate the stability of the electrocatalysts. As can be seen at the beginning of the Chronoamperometry curve, as time passes, the current density rapidly drops (I proportional to $t\text{-}^{1/2}$). The electrodes' inhibition by the products of the methanol oxidation reaction may be characterized by a decreasing rate over time. When comparing the prepared catalysts, PtRu/MWCNT binary catalysts and

PtRu(X)/MWCNT ternary catalysts the order of stability of the electroacatalysts to the Methanol electrooxidation is as follows PtRuW/MWCNT> PtRu/MWCNT >PtRuMo/MWCNT >PtRuIr/MWCNT.

5.3. CONCLUSION

According to this study, microwave assisted modified polyol catalyst preparation techniques were successfully used to synthesize the PtRu and PtRu(X) supported on MWCNT. Using XRD and HR-TEM, the synthesized electrocatalysts were found to have average particle sizes of 1.20nm-4.33 nm with crystalline sizes ranging from 1.36 to 4.96nm nm. According to the XRD study, the produced electrocatalysts exhibit PtRu, PtRuMo, PtRuIr, and PtRuW alloy phases. When compared to commercial PtRu/C electrocatalyst, it was discovered that the PtRuMo/MWCNT and PtRuIr/MWCNT demonstrated better electrocatalytic activity towards methanol oxidation with greater current density values.

In addition, when compared to other electrocatalysts, the PtRuMo/MWCNT electrocatalyst showed the highest current density for methanol oxidation and lowest onset potentail. This is explained by the fact that it has the smallest particle size of 1.20nm and is most conducive to the anodic oxidation process with the highest surface area of $180m^2/g$. The PtRuMo/MWCNT electrocatalyst demonstrated faster electrochemical reaction kinetics for the electrooxidation of methanol than the commercial PtRu/C catalyst with charge transfer resistance values of 1.045kΩ and 1.990kΩ respectively. However, the commercial PtRu/C catalyst showed better kinetics than the other three electrocatalysts from electrochemical impedance spectroscopy results. The chronoamperometry studies showed that PtRu/C commercial catalyst was the most stable electrocatalyst followed by ternary catalyst PtRuW/MWCNT.

Based on all the data gathered during the investigation, it was determined that the ternary PtRuMo, PtRuIr, and PtRuW electrocatalysts on MWCNT support produced better catalytic activity than the binary PtRu/MWCNT electrocatalyst. This was done by adding Mo, Ir, and W metallic additives to the PtRu metal alloy architecture using a microwave assisted modified polyol process of catalyst preparation. However, the commercial PtRu/C performed better than the binary PtRu/MWCNT and ternary PtRuW/MWCNT in the methanol oxidation reaction.

Ternary Catalyst PtRuMo/MWCNT performed better than binary PtRu/MWCNT and binary PtRu/C commercial catalysts despite having almost the same Platinum metal loading 21.64%, 21.37% and 20% respectively this is due to the presence of Molybdenum metal adding to the effect of byfunctional mechanism thereby enhancing splitting of water to the OH group to reduce CO poisoning of Platinum more efficiently. Based on all the results acquired in this study, it was concluded that adding a third metal to the binary metallic arthitecture of a PtRu electrocatalyst improves its performance and the microwave assisted process is a contributing factor[15].

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CHAPTER SIX

RESULTS AND DISCUSSIONS ON HEAT TREATED BINARY PtRu/MWCNT CATALYSTS

ABSTRACT:

This study investigated heat treated PtRu metal alloys supported on multi-walled carbon nanotubes (MWCNT) prepared by modified polyol method for methanol oxidation reaction (MOR) in acidic medium at 250^0C, 350^0C and 450^0C respectively. Catalysts were subjected to carefully control systematic heat treatment procedures and thoroughly investigated for their physical and electrochemical characterisations in acidic medium. HR-TEM and XRD techniques were used to determine the particle size and crystalline size of the electrocatalysts, respectively while Energy Dispersive Spectroscopy, EDS was used to determine elemental composition. XRD confirmed that the catalysts exhibit face-centered crystal structure characteristic of a pure platinum structure. High Resolution Transmission Electron Mi croscopy (HR-TEM) image showed spherical and agglomerated PtRu nanoparticles and narrow particle size distribution dispersed on the support materials. From HR-TEM, the particle sizes are in the range of 0.600nm to 1.005nm while the crystalline sizes from XRD ranged from 0.500nm to 1.180nm.

The electro-kinetics and stability of the electrocatalysts towards methanol in acidic medium were studied using electrochemical impedance spectrometry (EIS) and chronoamperometry (CA) respectively, while the cyclic voltammetry (CV) was used to determine the electroactive surface area (ECSA) and methanol oxidation reaction, MOR of the electrocatalysts.

PtRu/MWCNT electrocatalysts alloyed at 450^0C showed better electroactivity and kinetics towards methanol oxidation reaction (MOR) as compared to PtRu/MWCNT catalysts produced at 350^0C and 250^0C evident from the highest current density of 19.872mA/cm^2.and lowest charge transfer resistance of 0.151kΩ respectively compared to PtRu/MWCNT alloyed at different temperatures.

6.0 INTRODUCTION

Fuel cells have received a lot of interest among various energy technologies because of their high energy conversion rates, plentiful fuel supplies, and environmental friendliness [1, 2]. Fuel cells employ redox processes involving oxygen and fuels to transform chemical energy into electricity [3, 4]. Even though a lot of work has been done over the years, there are still some fundamental problems that need to be solved. Platinum is currently the most well-known MOR catalyst, and significant efforts have been made to increase its activity and usage. Pt-based catalysts have got several disadvantages including their high cost and sensitivity to impurities. The main method in this study is alloying platinum with ruthenium metal using the modified polyol method of catalyst preparation and afterwards the resulting nanoparticles were heat treated at higher temperatures to improve the methanol elecrooxidation reaction [5–7]. Heat treatment with respect to Pt-based catalysts can induce particle-size growth, a better alloying degree, and changes in the surface morphology of the catalyst from amorphous to more ordered states, all of which will have a remarkable effect on their electroactivity and stability. [8]

The impact of heat treatment on Pt catalysts has been extensively studied [8]. In this study the binary PtRu/MWCNT catalysts synthesized by the modified polyol method are heat treated at 250^0C, 350^0C and 450^0C to examine the impact of the heat treatment on their morphology, particle size, electroactivity and stability towards methanol electrooxidation.

According to a study by Valisi et. al [9] It was concluded that heat treatment of fuel cell catalysts plays an important role in the improvement of ORR electrocatalytic activity and stability. The best ORR activity was noted in the order Pt-Cu/C (T, 350 °C)>Pt-Fe/C (T, 350 °C)>Pt-Ni/C (T, 350 °C)>Pt-Co/C (T, 250 °C)>Pt/C (T, 350 °C).

Xiowel et al. [10] used a simple deposition of Au metal on a commercial PtRu/C catalyst followed by heat treatment at three different temperatures to prepare carbon supported Au-PtRu catalysts as anodic catalysts for DMFC. Simple deposition of Au particles on a commercial Pt-Ru/C catalyst was followed by heat treatment of the resulting composite catalyst at 125, 175, and 200 degrees Celsius in a N atmosphere. The electrocatalytic stability of Au-PtRu/C catalysts heat-treated at 175 °C was found to be the highest among heat-treated catalysts.

In another study [11] heat treatment induced a high degree of alloying on the PtM/C (M=Cr, Pd, Co) and a high electrical conductivity of the electrode but caused agglomeration of Pt particles. In addition, PtCo/C exhibited the highest performance in a PEM fuel cell providing a current density of around 392.8mA/Cm^2.

The advantages of heat treatment include the removal of any undesirable impurities that may have resulted from the early stages of preparation. Heat treatment also improves the electro-catalytic activity of the synthesized catalyst by allowing for uniform dispersion and stable distribution of the metal on the support [12, 13]. Heat treatment has a significant impact on metal particle size and distribution, particle surface morphology, and metal dispersion on the support. Particle growth in the catalyst during heat treatment of Pt and its alloys can lead to increased activity and durability [13]. Heat treatment of Pt catalyst, according to Jalan et al [14], lowers the dissolution rate as well as the initial surface area. The fundamental properties of the catalyst and its support are also affected by heat treatment, including the number of catalytic sites, the distribution of the catalyst particle on the support, the loading level of the catalyst on the support, and the acid-base properties of the support [12, 13].

There are different types of heat treatment methods used such as the oven/furnace heating, microwave heating, plasma thermal heating, and ultrasonic spray pyrolysis. Among all these the oven/furnace heating method is widely used. Catalysts using carbon black as support for the catalytic metal, the heat treatment process is understood to provide two main functions for the stability, the removal of oxygenated functional groups and graphitization of the carbon support surface. The carbon surface of most carbon blacks is functionalized with various oxygen-containing functionalities which affect the surface chemistry of the carbon support [15].

The carbon black (Vulcan XC72R)-supported palladium–vanadium electro-catalysts were heat treated at a range of temperatures in 10% H2 in Ar and the effect of heat treatment on particle morphology was studied and the results showed that the particle size increased at high temperatures. It was also found that the catalyst showed enhancement in the electrocatalytic activity after heat treatment [16]

6.1 METHODOLOGY

6.1.1 PREPARATION OF BINARY CATALYST PtRu/MWCNT

The PtRu bimetallic nanoparticle catalysts were supported onto the walls of MWCNTs by firstly using the modified polyol reduction method before heat treatment

6.1.1.1 MODIFIED POLYOL METHOD

Catalysts were prepared by following the procedures of Jeng et al. [17] and L. Khotseng et al [18] methods of Platinum based binary catalyst synthesis with little modifications. Ethylene glycol (EG) which acts both as the reducing agent and stabilizer [19] was chosen because of its inherent advantages which include the homogeneous distribution and small particle size [19, 20]

1. 75mg of MWCNTs was added to 60ml ethylene glycol (EG) for ratio of (1:1) the mixture was sonicated for 15mins and stirred at room temperature for 30mins to form a homogenous paste.

2. In a separate beaker, PtRu (1:2 atomic ratio) was prepared with a calculated amount of 0.0772mmol of $H_2PtCl_6 \cdot 6H2O$ and 0.1544mmol of $RuCl_3$ used as Pt and Ru precursor salts respectively, were added and dissolved in a 3:1 ratio of ethylene glycol and stirred at room temperature to obtain a uniform mixture.

3. The salt/EG solution was then added to MWCNT/EG paste and the pH adjusted to about 3.6 by adding drop-wise suitable amounts of 4 M NaOH.

4. The resultant mixture was subjected to high-speed stirring for 1 hour for the metal salts to adhere to the surface of MWCNTs. After that, the mixture was refluxed for 3 h at 160 °C under continuous flow of nitrogen; it was then left to cool down and then washed with ultra-pure water.

5. Finally, the mixture was then filtrated and the residue (PtRu/MWCNT nanoparticle) was oven-dried at 60 °C overnight and PtRu/MWCNT catalyst will be obtained.

6.1.1.2 HEAT TREATMENT OF THE CATALYSTS

PtRu/MWCNT binary catalysts synthesized using the modified polyol process were heat treated at various temperatures under temperature control. The morphology and activity of the catalysts, as well as their uniform distribution on the catalytic support, are affected by heat treatment. The tube furnace had already been preheated to the desired temperature. The catalyst was placed in an alumina boat in the center of the tube furnace. The catalyst was heated for 3 hours at various target temperatures of 250^0C, 350^0C, and 450^0C while nitrogen flowed at a rate of 5 ml/min. When the heating time was up, the tube was cooled while the nitrogen gas continued to flow at a constant rate of 5 ml/min, and the catalyst was removed from the furnace.

6.2 RESULTS AND DISCUSSION

6.2.1 Structural Characterization of heat treated PtRu/MWCNT @450^0C , PtRu/MWCNT @350^0C and PtRu/MWCNT @250^0C electrocatalysts.

Energy-dispersive X-ray spectroscopy (EDS) was utilized to determine the metal loading of the electrocatalysts before the heat treatment. Binary catalyst PtRu/MWCNT prepared by the modified polyol method has a Pt wt.% of 2.35 and a Ruthenium wt.% of 5.80. All catalysts present atomic ratios that are comparable; the information about the microstructure of the prepared electrocatalysts was determined using HR-TEM and XRD.

Crystallite sizes of the electrocatalysts were calculated using Scherrer's equation and particle sizes obtained using high-resolution transmission electron microscopy (HR-TEM). The crystalline size of the metal particles is calculated using Debye- Scherrer's equation, $K\alpha/\beta\text{Cos}\theta$, Where K, Scherrer constant, $\alpha = 0.9$, X-Ray wavelength =0.154nm. $\beta(2\theta)$, the width of the diffraction peak (rad). The particle size determined by HR-TEM was obtained using Image J software (Image Processing and Analysis in Java developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation LOCI, University of Wisconsin, Madison, WI, USA) over multiple areas for each electrocatalyst.

Table 6. 1: Properties of the Pt-Ru/MWCNT@ 250^0C, Pt-Ru/MWCNT@ 350^0C and Pt-Ru/MWCNT@ 450^0C Catalysts;

ELECTROCATALYSTS	Crystalline size(nm)	Particle size(nm)	ECSA
PtRu/MWCNT 250^0	1.178	1.005	5.098m^2/g
PtRu/MWCNT 350^0	0.596	0.616	3.922m^2/g
PtRu/MWCNT 450^0	0.595	0.600	16.714m^2/g

XRD confirmed that all PtRu/CNTelectrocatalysts heat treated@250^0C,350^0Cand450^0C exhibit the face-centred cubic (fcc) crystallines structures with PtRu/CNT@450deg having smallest crystalline size. The X-ray diffraction (XRD) results is a perfect resemblance of the Pt catalyst X-ray diffraction pattern of Bragg`s angles of 39.76^0, 46.2^0, 67.4^0, 81.3^0 and 85.7^0 correspond to (111),(200), (220) and (311) and (222) respectively. The Bragg angles indicate that the heat treatment had effects on bimetallic architecture of the PtRu crystals.

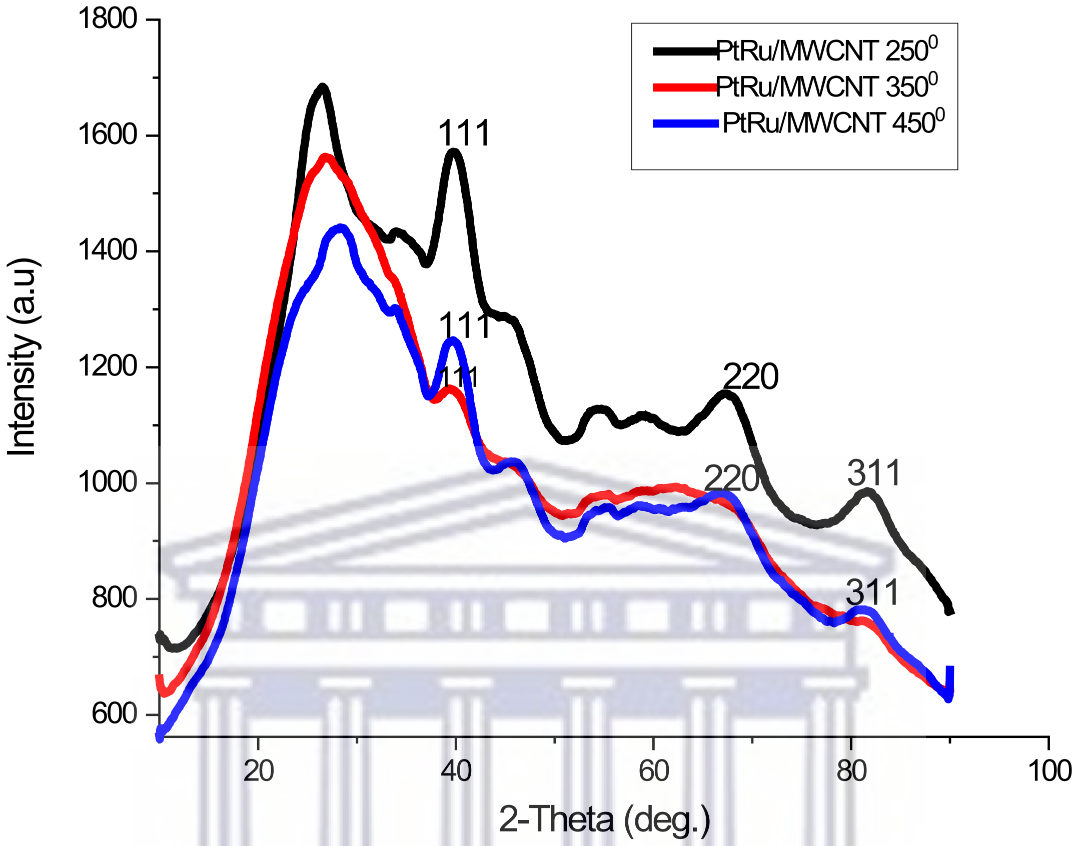

Figure 6. 1: XRD spectra of PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@450^{0}C electrocatalysts supported on MWCNTs

Fig. 6.2 is the HRTEM micrographs of PtRu electrocatalysts on MWCNT heat treated at 250^{0}C, 350^{0}C and 450^{0}C respectively. Catalyst nanoparticle are the dark dots. Multi-walled carbon nanotubes (MWCNTs) support are the large tube-like particles seen, with diameter is about 20 nm. The PtRu nanoparticles got more agglomerated on the MWCNT as temperature increases indicating that the heat treatment made the particles of the electrocatalyts to get more closely packed.

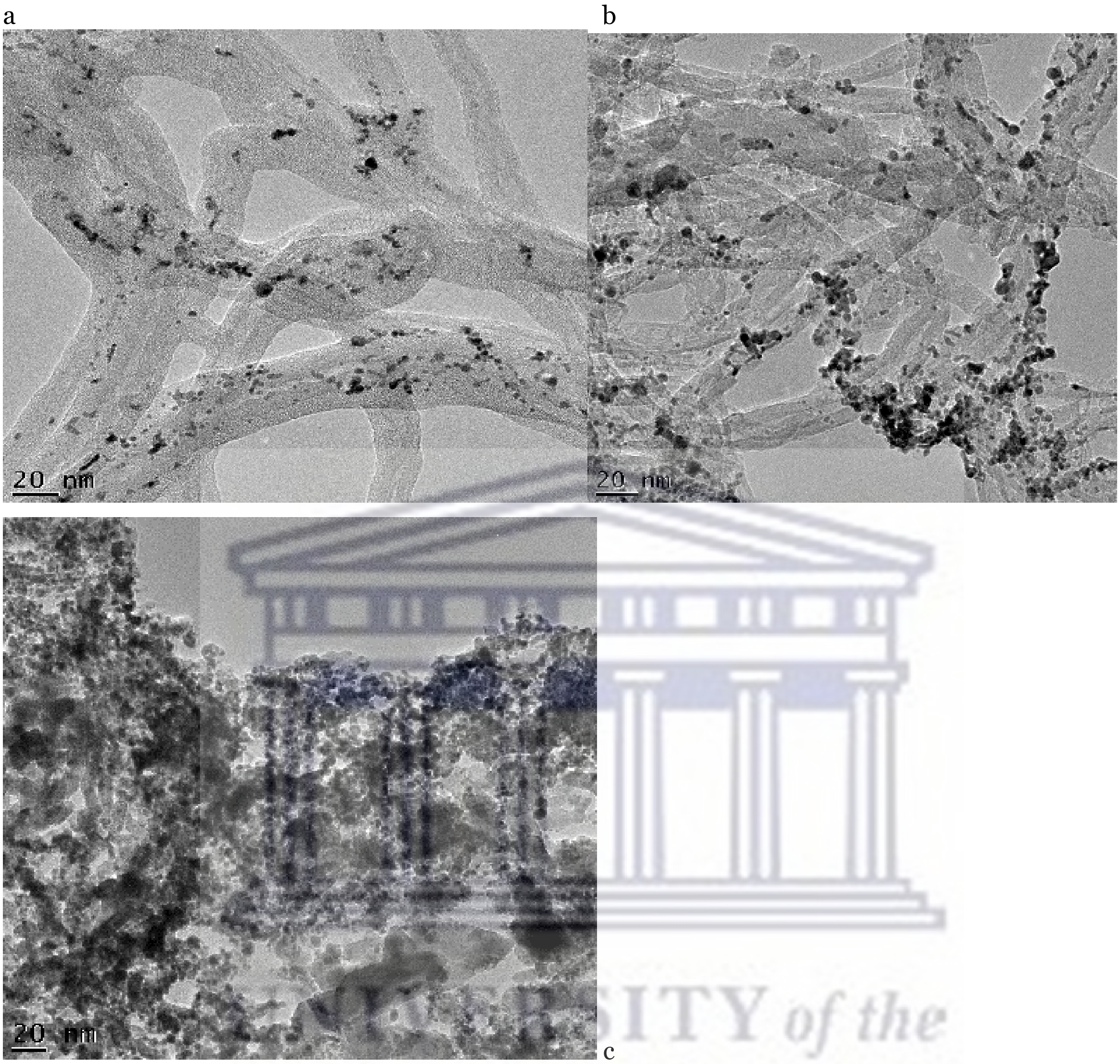

Figure 6. 2 / Scale: 20nm: HR-TEM micrographs of a) PtRu/MWCNT @250^{0}C, b) PtRu/MWCNT @350^{0}C) PtRu/MWCNT @450^{0}C

6.2.2 Evaluation of electrocatalytic activity for PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@450^{0}C electrocatalyts.

Cyclic voltammetry was used to initially assess the electrochemical activity of the produced catalysts in a 0.5 M HClO4 solution. The adsorption peaks for the various catalysts could be seen from the cyclic voltammetry of the electrocatalysts that had been synthesized. Equation (1) was used to calculate the electro-active surface area of the catalysts using the peak area of the adsorption peak of the electrocatalysts in cyclic voltammetry [21]

$$ECSA = \frac{Q}{210\mu C/cm2.m.Ag} \qquad (6)$$

Ag is the geometric surface area of the electrode (5 mm in diameter), Q is the charge from the adsorption peak of in Coulomb taking within in negative potential region -0.2 V to 0.08 V in the forward scan, and 210 μ Ccm^{-2} is the value for the charge of full coverage for clean polycrystalline Pt monolayer [22]

The obtained ECSA values are 16.71m^2/g for PtRu/MWCNT@450^{0}C, 3.92m^2/g for PtRu/MWCNT@350^{0}C and 5.098 m^2/g for PtRu/MWCNT@250^{0}C. Higher ECSA value of 16.710 m^2/g for PtRu/MWCNT@450^{0}C can be attributed to its improved alloying with lowest particle size value of 0.600nm.

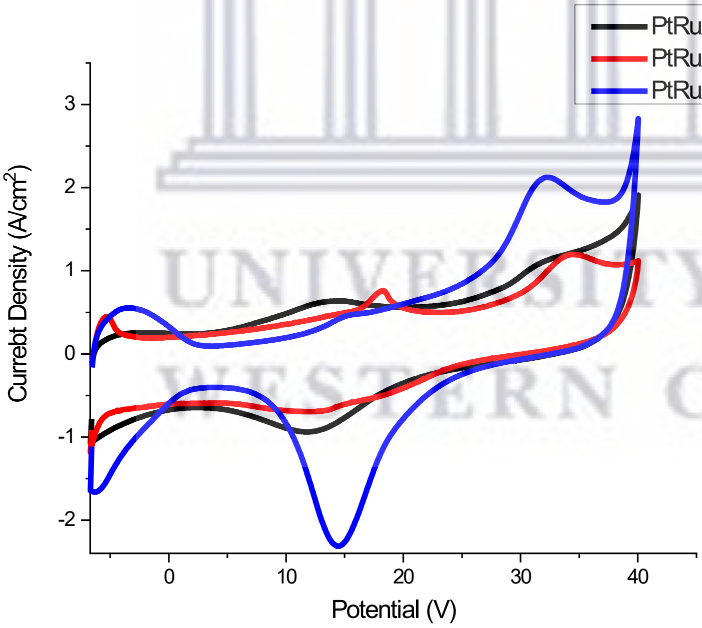

Figure 6. 3: Cyclic voltammograms of PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@450 °C electrocatalysts in N_2 saturated 0.5 M Perchloric acid, $HClO_4$ at a scan rate of 30mVs^{-1}

6.2.3. Comparison of Methanol Oxidation on PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@450^{0}C electrocatalyts in 0.5M Perchloric acid solution at a scan rate of 30mVs^{-1}

The electrocatalytic activity towards methanol oxidation are summarized in Table 3. By comparing the characteristics of the CVs, the increment in temperature in the metal alloys was found to substantially enhance the catalytic activity for methanol electrooxidation. First, the onset potentials (measure of catalytic activity) of methanol oxidation for the heat treated PtRu/MWCNT catalyst at 250^{0}C showed relatively lower values than that of other electrocatalysts. The positions of the onset potentials follow the order of PtRu/MWCNT@450^{0}C >PtRu/MWCNT@350^{0}C >PtRuW/MWCNT@250^{0}C. The forward peak current densities (measure of the maximum catalyst performance) of the binary catalyst PtRu/MWCNT took the order PtRu/MWCNT@450^{0}C >PtRu/MWCNT@250^{0}C >PtRuW/MWCNT@350^{0}C.

Thus, the binary catalyst PtRu/MWCNT@450^{0}C exhibited best electrochemical performance in terms of the highest forward peak current density followed PtRu/MWCNT@250^{0}C.

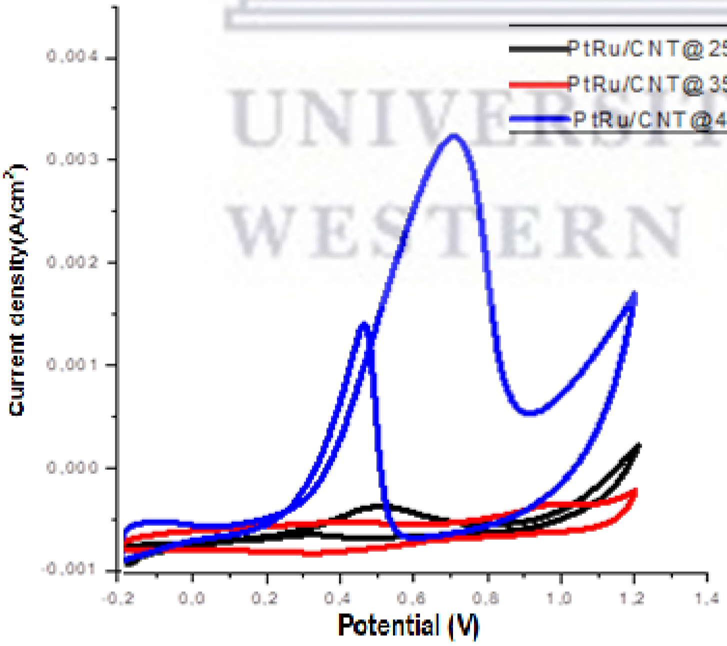

Figure 6. 4: Cyclic voltammograms of PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@450^{0}C electrocatalysts in N_2 saturated 0.5 M Perchloric acid, $HClO_4$ and 2M Methanol at a scan rate of 30mVs^{-1}

Table 6. 2: Comparison of the electrocatalytic activity of the catalysts for Methanol Oxidation

ELECTROCATALYSTS	Onset-Potential(V)	Current Density(mA/cm^2)	Mass Activity{A/g]
PtRu/MWCNT 250^0	0.0841	1.343	13.17
PtRu/MWCNT 350^0	-0.194	0.602	5.90
PtRu/MWCNT 450^0	-0.198	1.987	19.48

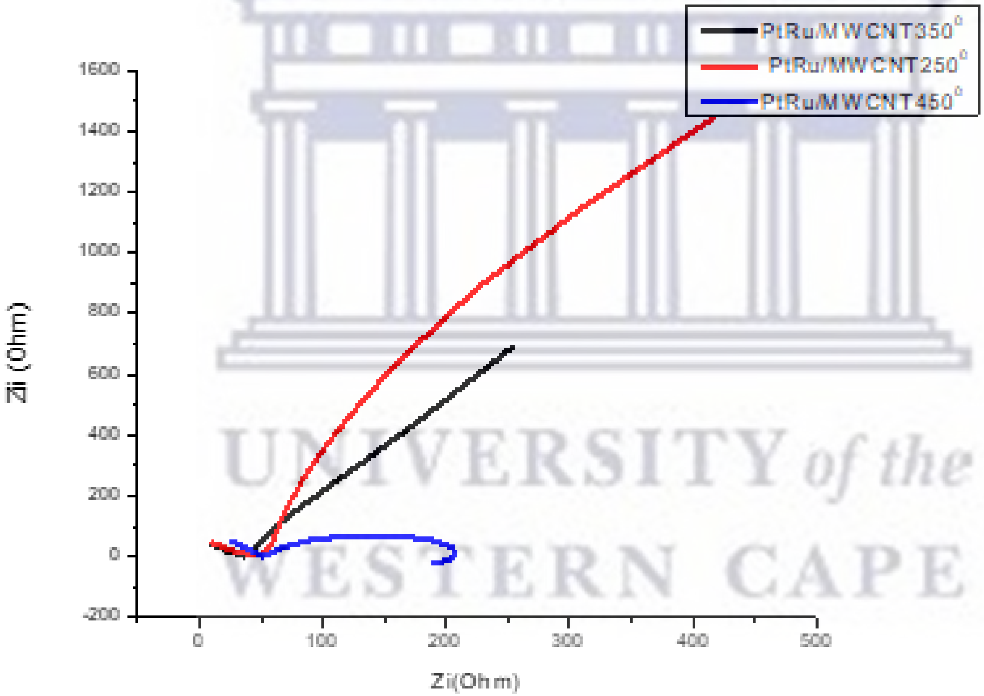

Figure 6. 5: Electrochemical impedance curves of methanol oxidation on heat treated PtRu/MWCNT electrocatalysts in N_2 saturated 0.5M HClO4 and 0.2M Methanol

Electrochemical impedance spectroscopy technique was used to investigate the catalytic reaction kinetics for the methanol oxidation on the anodic PtRu/MWCNT@250^{0}C, PtRu/MWCNT@350^{0}C and PtRu/MWCNT@250^{0}C electrocatalysts surfaces. The charge transfer resistance, Rct values using Equivalent Circuit fitting were 0.151kΩ, 2.04kΩ and

11.31kΩ for PtRu/MWCNT@450⁰C, PtRu/MWCNT@350⁰C and PtRu/MWCNT@250⁰C respectively indicating that PtRu/MWCNT@450⁰C exhibited best kinetics towards the methanol electrooxidation with the best conductivity to flow of electric current.

Table 6. 3: Charge Transfer Resistance of PtRu/MWCNT electrocatalysts

ELECTROCATALYSTS	CHARGE TRANSFER RESISTANCE(R_{CT})
PtRu/MWCNT 250⁰C	11.31kΩ
PtRu/MWCNT 350⁰C	2.040kΩ
PtRu/MWCNT 450⁰C	0.151kΩ

PtRu/MWCNT heat treated at 450⁰ gave best kinetics as it offered least resistance to the flow of current with charge transfer resistance value of 0.151kΩ followed by PtRu/MWCNT heat treated at 350⁰C.

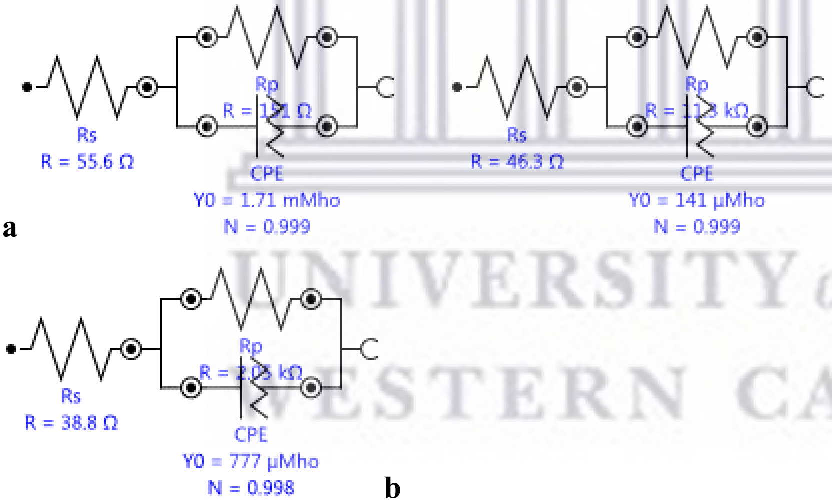

Figure 6. 6: Equivalent circuits for the electrochemical impedance spectroscopy of methanol oxidation on (a) PtRu/MWCNT@450⁰C, (b) PtRu/MWCNT@350⁰C and (c) PtRu/MWCNT@250⁰C electrocatalysts in N_2 saturated 0.5M HClO4 and 0.2M Methanol.

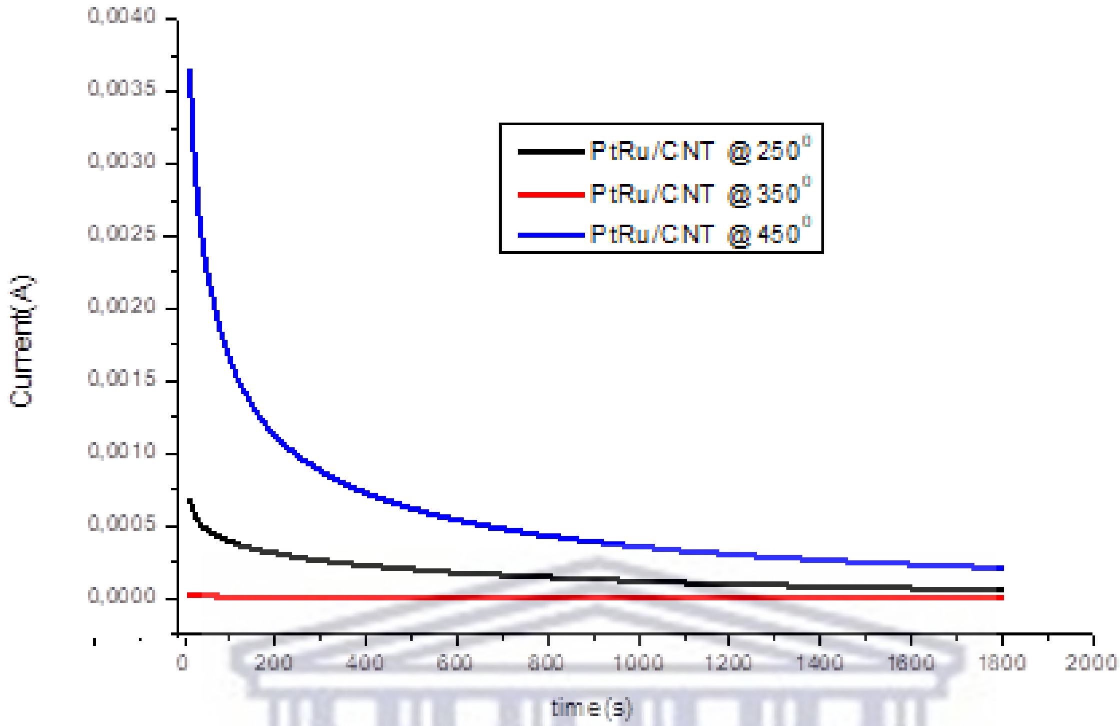

Figure 6. 7**:** The Chronoamperometry Curves of methanol oxidation on heat treated PtRu/MWCNT electrocatalysts in 0.5M $HClO_4$ and 2.0M CH_3OH.

For the electrocatalysts to be used effectively in DMFCs, stability is vital. In N_2 saturated 0.5M HClO4 with 2.0M methanol, Figure 5 displays the chronoamperometry (CA) of PtRu/MWCNT electrocatalysts on MWCNT support. This was done to evaluate how well the various catalysts held up after 1800 seconds. As can be seen at the beginning of the Chronoamperometry curve, as time passes, the current density rapidly drops (I proportional to $t\text{-}^{1/2}$). The electrodes' inhibition by the products of the methanol oxidation reaction may be characterized by a decreasing rate over time. When comparing the prepared catalysts, PtRu/MWCNT binary catalysts heat treated at different temperatures the order of stability of the electroacatalysts to the methanol electrooxidation is as follows PtRu/MWCNT @450^{0}C> PtRu/MWCNT@250^{0}C >PtRu/MWCNT @350^{0}C from their current density values of 0.284mA/cm^2

Table 6. 4: Current density values from the chronoamperometry curve for the stability test of the PtRu/MWCNT electrocatalysts.

ELECTROCATALYSTS	Current Density(mA/cm^2)
PtRu/MWCNT 250^0	0.284
PtRu/MWCNT 350^0	0.0329
PtRu/MWCNT 450^0	1.296

6.4 CONCLUSION

In this study, PtRu, supported on MWCNT, was successfully synthesized with the modified polyol method and heat treated at 250^0C. 350^0C, 450^0C respectively. The synthesised electrocatalysts had crystalline sizes of 0.595–1.178 nm and average particle sizes of 0.699–1.005 nm, determined using XRD and HRTEM, respectively. The PtRu alloy phase is a perfect resemblance of the Pt catalyst structure according to XRD analysis. It is found that the PtRu/MWCNT electrocatalyst heat treated at 450^0C showed enhanced electrocatalytic activity towards methanol oxidation compared to other PtRu electrocatalysts on MWCNT support with a mass activity of 19.48A/g. Furthermore, the 450^0C PtRu/MWCNT electrocatalyst had the largest current density for methanol oxidation compared to other electrocatalysts. This can be attributed to it having the smallest particle size and being the most active towards anode oxidation reaction. From the EIS, it was concluded that the PtRu/MWCNT electrocatalysts at 450^0C exhibited a faster electrochemical reaction kinetics than both PtRu/MWCNT electrocatalysts heat treated at 250^0C and 350^0C with a charge transfer resistance value of 0.151kΩ.

Finally, the temperature 450^0C was found to be optimal as the PtRu/MWCNT electrocatalyst heat treated at this temperature is also the most stable electrocatalyst followed by the PtRu/MWCNT electrocatalyst heat treated at 250^0C as shown by the chronoamperomerty tests.

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CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Four catalyst preparation methods, namely Impregnation, polyol, modified polyol and microwave assisted modified polyol methods were used to synthesize binary PtRu/MWCNT catalyst. Microwave assisted modified polyol method proved to be the best preparation method as it produced PtRu/MWCNT catalyst with best electroactivity, kinetics and stability to methanol oxidation reaction. The modified polyol synthesized catalysts which were also promising for the methanol electrooxidation were also heat treated at 250^0C,350^0C and 450^0C for optimisation. Temperature of 450^0C was the optimum temperature as it produced electocatalysts with highest current density and kinetics to the methanol electrooxidation.

Ternary catalysts PtRuIr/MWCNT, PtRuMo/MWCNT and PtRuW/MWCNT were also synthesized by the microwave assisted modified polyol method. Furthermore, when compared to other electrocatalysts, the PtRuMo/MWCNT electrocatalyst demonstrated the highest current density and lowest onset potential for methanol oxidation. This is explained by the fact that it has the smallest particle size of 1.20nm and the highest surface area of 180m^2/g for anodic oxidation. The PtRuMo/MWCNT electrocatalyst demonstrated faster electrochemical reaction kinetics for the electrooxidation of methanol than the commercial PtRu/C catalyst and the two ternary catalysts, PtRuIr/MWCNT and PtRuW/MWCNT with charge transfer resistance value of 1.045kΩ. The chronoamperometry studies revealed that the commercial PtRuW/C catalyst was the most stable electrocatalyst.

The ternary PtRuMo, PtRuIr, and PtRuW electrocatalysts on MWCNT support produced better catalytic activity than the binary PtRu/MWCNT electrocatalyst, based on all the results from this investigation. This was accomplished by incorporating Mo, Ir, and W metallic additives into the PtRu metal alloy architecture via a microwave assisted modified polyol catalyst preparation process. In the methanol oxidation reaction, however, commercial PtRu/C outperformed binary PtRu/MWCNT and ternary PtRuW/MWCNT.

Despite having nearly the same Platinum metal loading (21.64%, 21.37%, and 20%, respectively), Ternary Catalyst PtRuMo/MWCNT performed better than binary

PtRu/MWCNT and binary PtRu/C commercial catalysts. This is due to the presence of Molybdenum metal adding to the effect of byfunctional mechanism, thereby enhancing splitting of water to OH group to reduce CO poisoning of Platinum more efficiently. Based on the findings of this study, it was concluded that adding a third metal to the binary metallic architecture of a PtRu electrocatalyst improves its performance, and that the microwave assisted process played a supporting role.

RECOMMENDATIONS FOR FUTURE WORK

1. Perform CO-Stripping CV electrochemical analysis on the catalysts synthesized to calculate ECSA to compare with the ECSA values got in this study using the adsorption peaks of the Cyclic voltammogram.

2.The PtRuXY/MWCNT quartenary catalysts should be prepared by the microwave assisted polyol method and characterized electrochemically.

3. Ternary Catalysts, PtRuIr/MWCNT, PtRuMo/MWCNT and PtRuMo/MWCNT synthesized can be heat treated at the optimum temperature(450^{0}C) and characterized electrochemically.

APPENDIX A1; Cyclic voltammograms of binary PtRu/MWCNT electrocatalysts produced by different synthesis methods in N_2-saturated 0.5 M perchloric acid $HClO_4$ at a scan rate of 30mV.s^{-1}

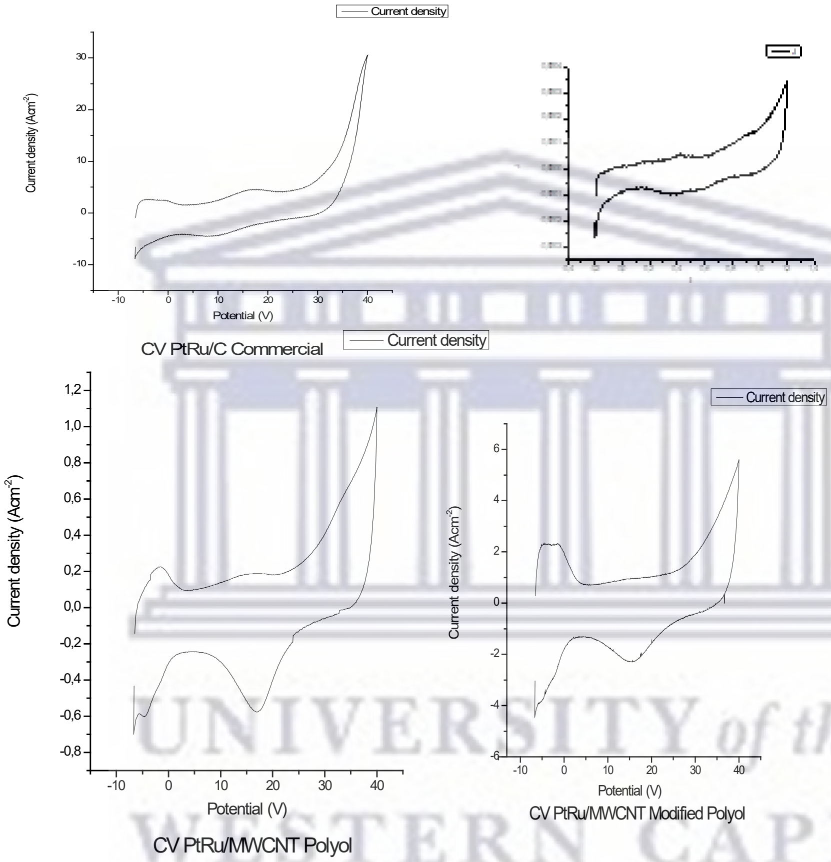


Figure A 1: Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N_2-saturated 0.5 M perchloric acid $HClO_4$ at a scan rate of 30mV.s^{-1}

APPENDIX A2; Cyclic voltammograms of binary PtRu/MWCNT and Ternary PtRu(X)/MWCNT catalysts electrocatalysts in N_2 saturated 0.5 M Perchloric acid. $HClO_4$ at a scan rate of 30mV.s^{-1}

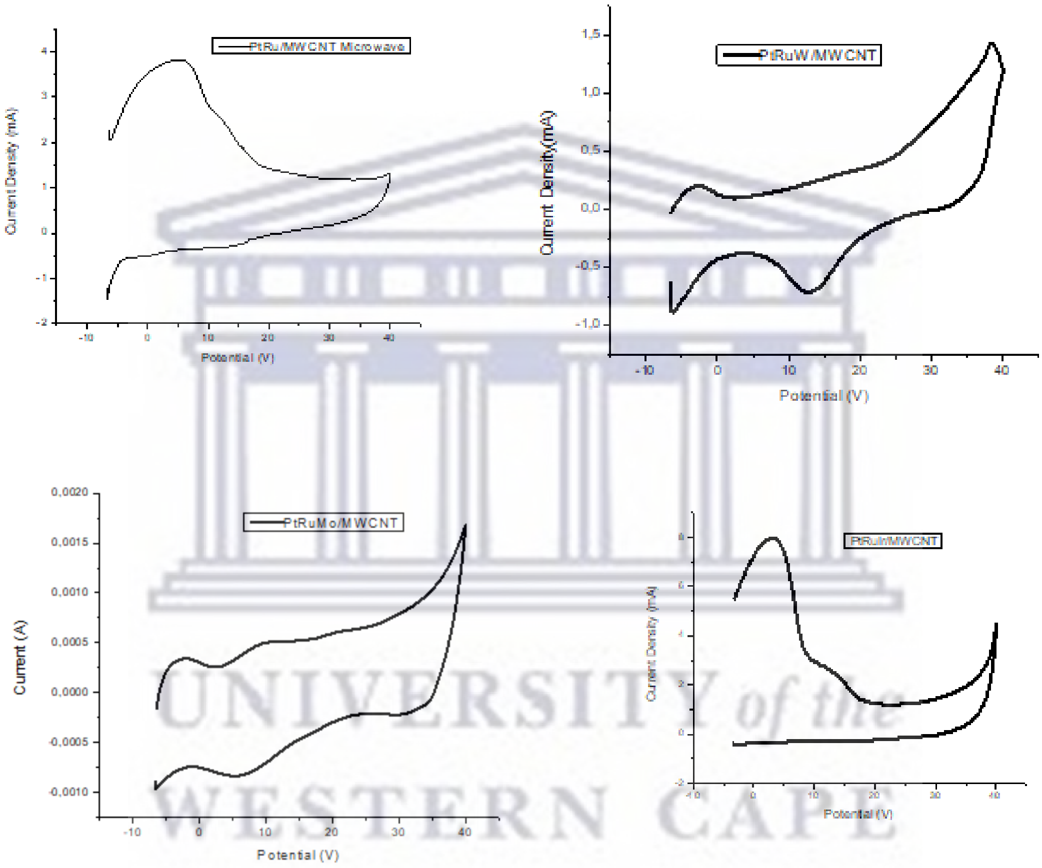
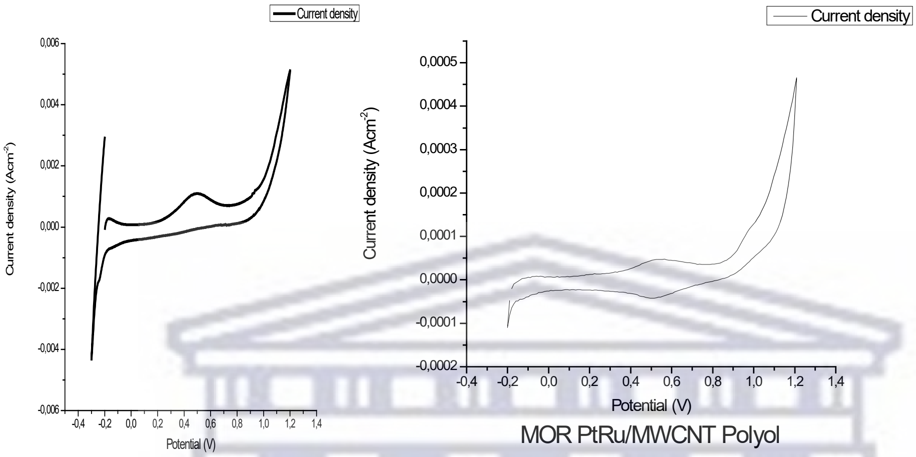


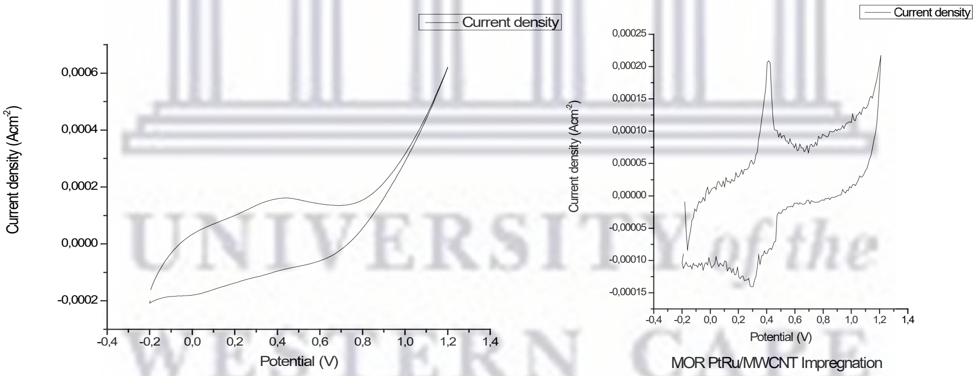
Fig. A 2. Cyclic voltammograms of PtRu/MWCNT and PtRu(X) catalysts electrocatalysts in N_2 saturated 0.5 M Perchloric acid. $HClO_4$ at a scan rate of 30mV.s^{-1}

APPENDIX A3; Cyclic voltammograms of binary PtRu/MWCNT electrocatalysts in N_2-saturated 0.5 M perchloric acid $HClO_4$ and 2 M methanol at a scan rate of 30mV.s^{-1}



MOR PtRu/MWCNT Polyol

MOR PtRu/C commercial



MOR PtRu/MWCNT Impregnation

MOR PtRu/MWCNT Modified Polyol

Figure A 3: Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N_2-saturated 0.5 M perchloric acid $HClO_4$ and 2 M methanol at a scan rate of 30mV.s^{-1}

APPENDIX A4; Cyclic voltammograms of binary PtRu/MWCNT and Ternary PtRu(X) catalysts electrocatalysts in N_2 saturated 0.5 M Perchloric acid. $HClO_4$ and 2M Methanol at a scan rate of 30mV.s^{-1}

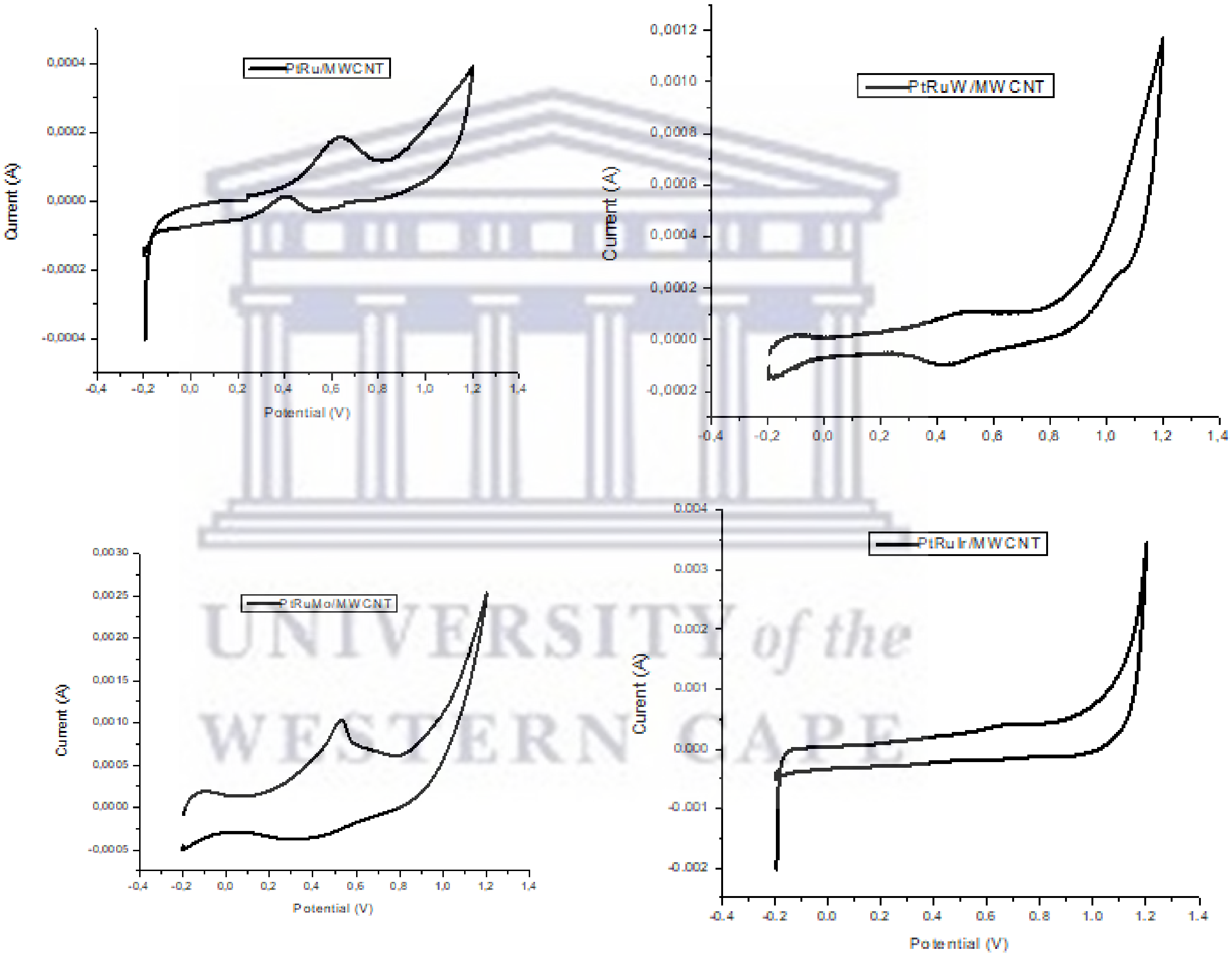


Fig. A 4. Cyclic voltammograms of PtRu/MWCNT and PtRu(X) catalysts electrocatalysts in N_2 saturated 0.5 M Perchloric acid. $HClO_4$ and 2M Methanol at a scan rate of 30mV.s^{-1}

APPENDIX A5; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on ternary PtRuIr/MWCNT electrocatalyst.

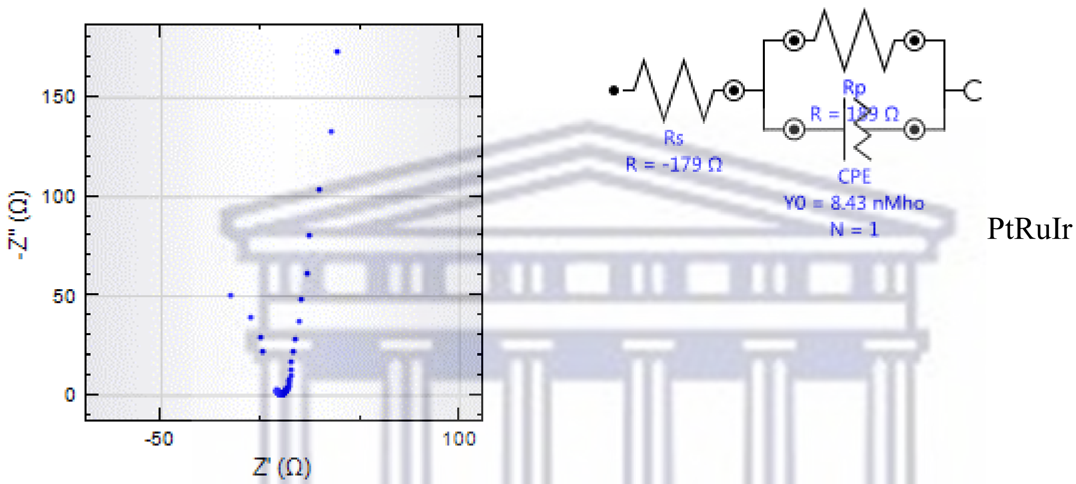
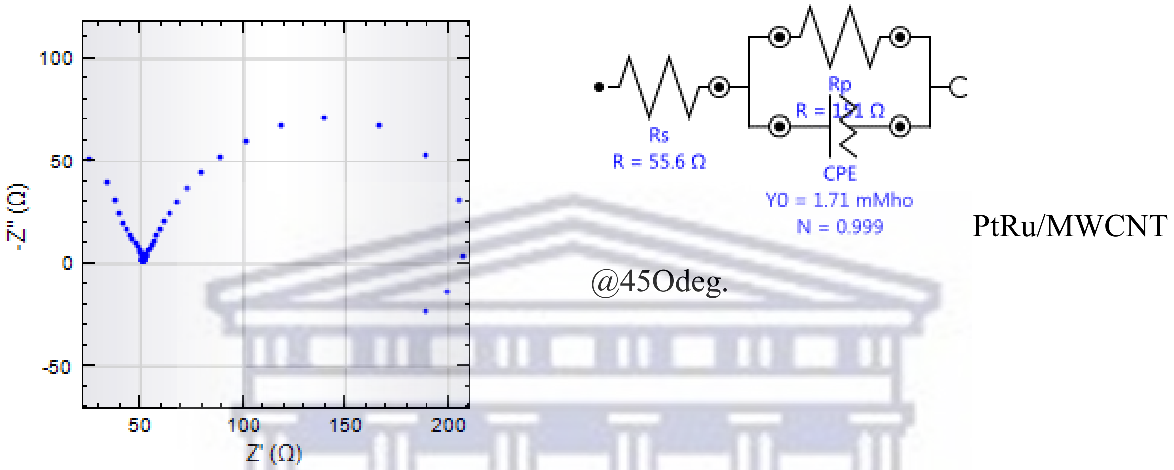


Fig. A 5. Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRuIr/MWCNT electrocatalyst.

APPENDIX A6; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst @ 450^0C

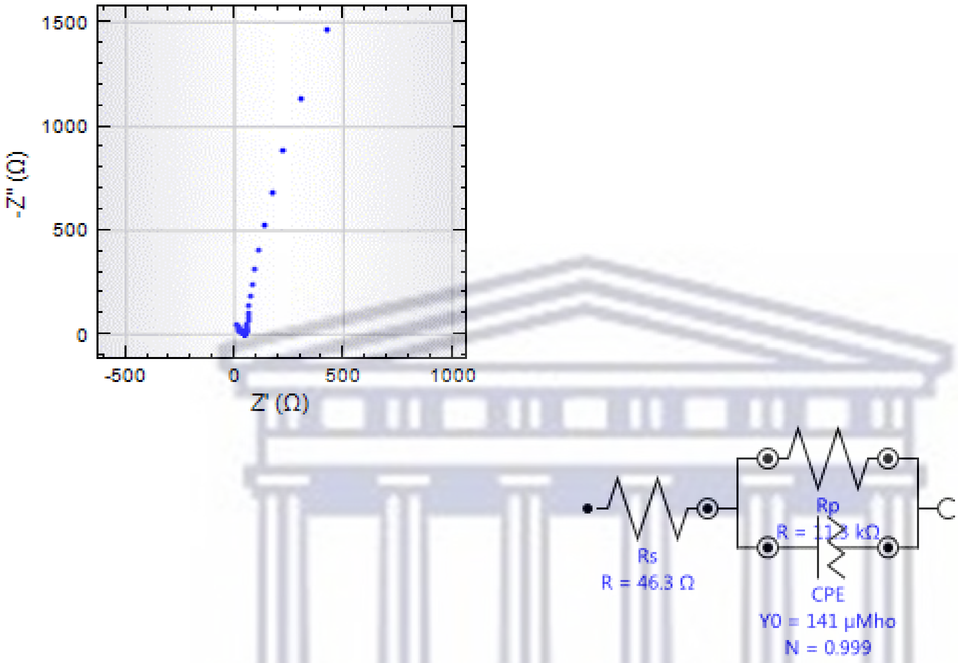


PtRu/MWCNT

@45Odeg.

Fig. A 6. Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst @ 450^0C

APPENDIX A7; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst @ 250^{0}C



PtRu/MWCNT

250deg

Fig. A 7. Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst @ 250^{0}C

APPENDIX A8; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst @ 350^{0}C

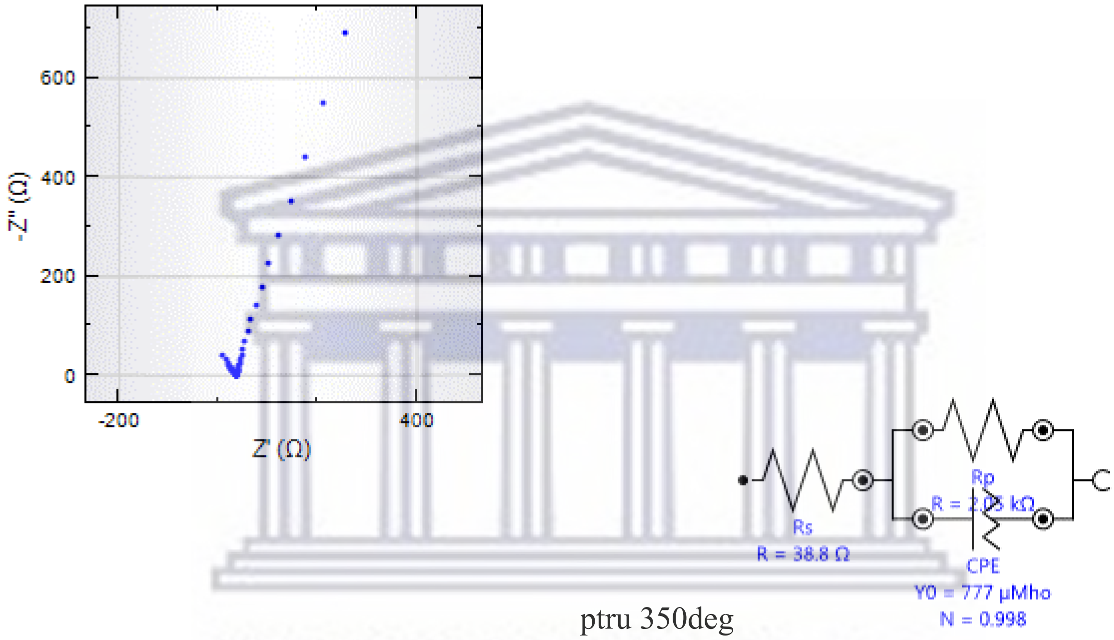
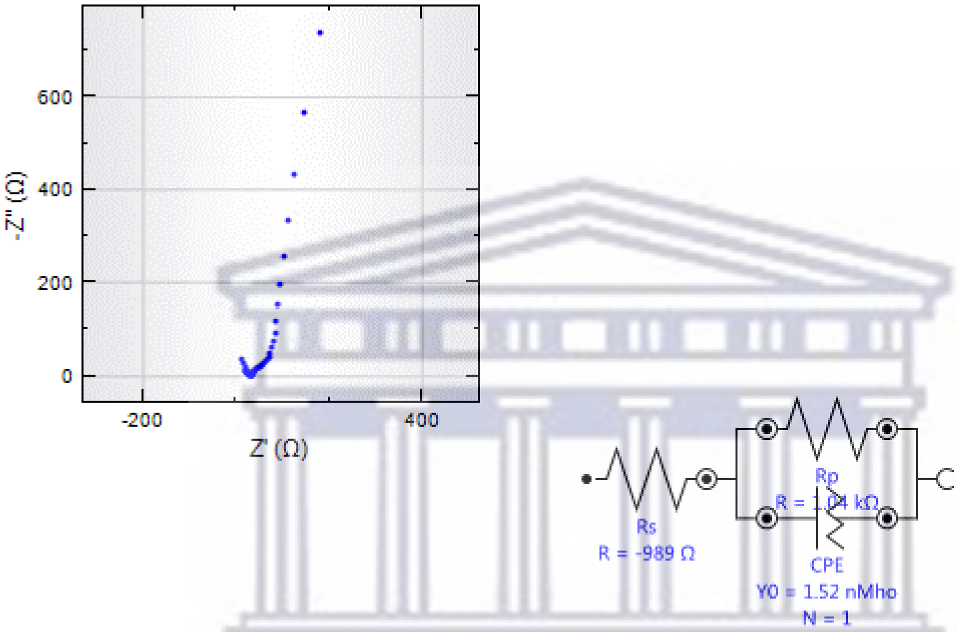


Fig. A 8. Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst @ 350^{0}C

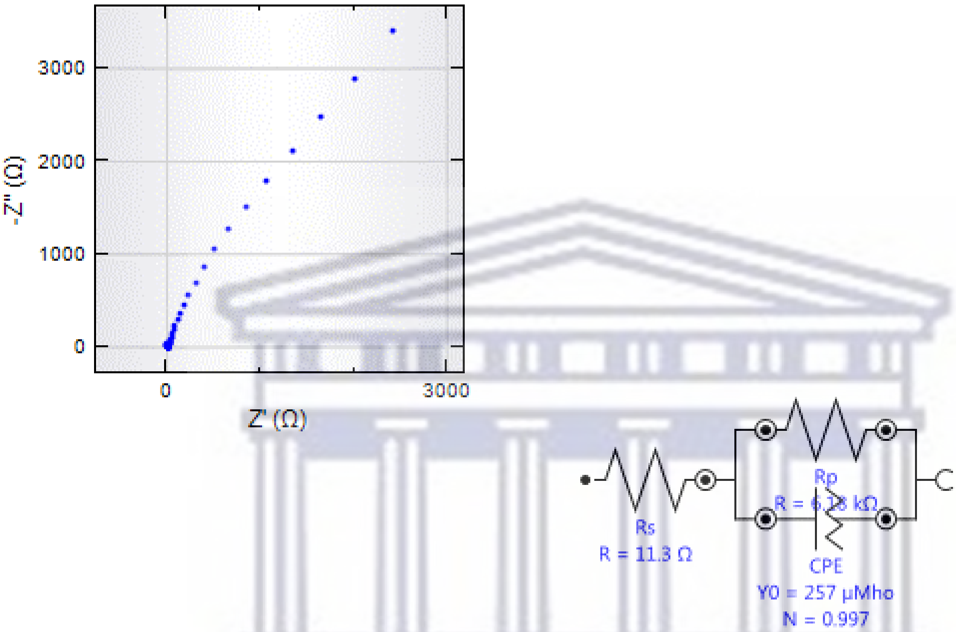
APPENDIX A9; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on ternary PtRuMo/MWCNT electrocatalyst.



ptrumo

Fig. A 9. Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRuMo/MWCNT electrocatalyst.

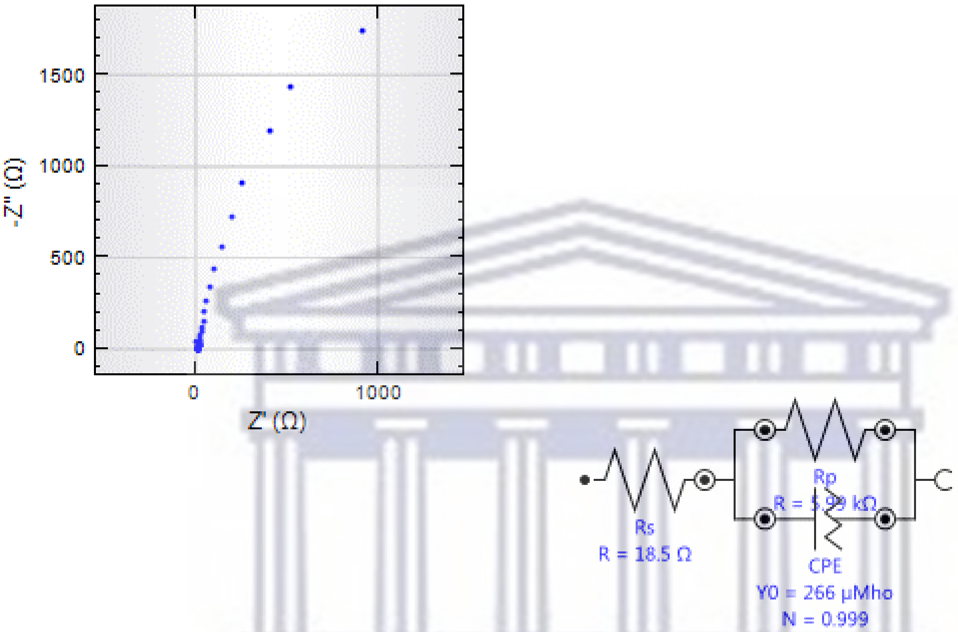
APPENDIX A10; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst produced by microwave assisted modified polyol method.



ptru microwave

Fig. A 10; Nyquists plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst produced by microwave assisted modified polyol method.

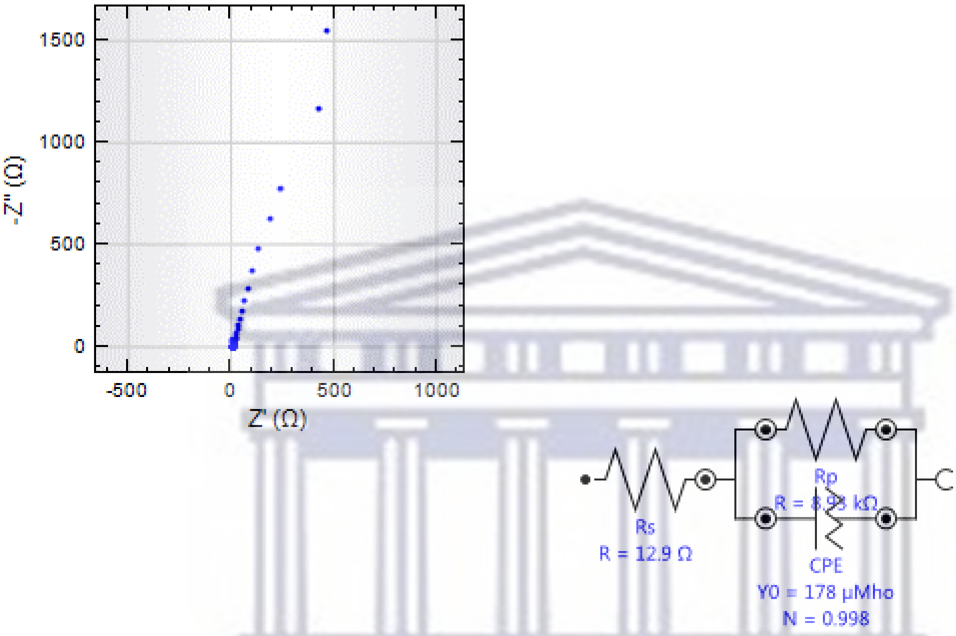
APPENDIX A11; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst produced by modified polyol method.



ptru modpoly

Fig. A 11; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst produced by modified polyol method.

APPENDIX A12; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst produced by polyol method.



ptru polyol

Fig. A 12; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst produced by polyol method.

APPENDIX A13; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/C commercial electrocatalyst..

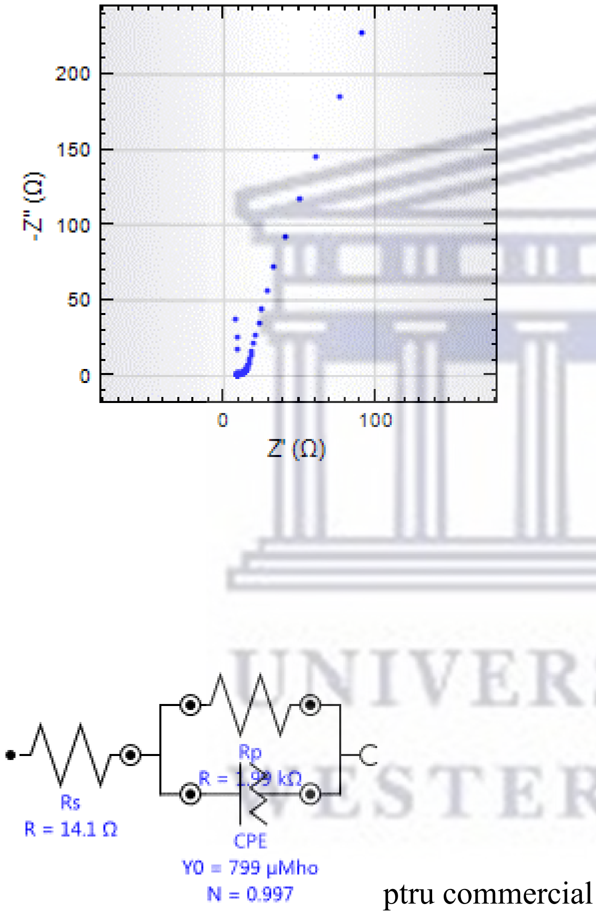
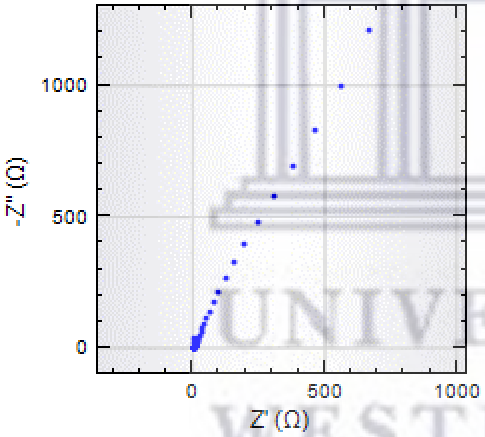
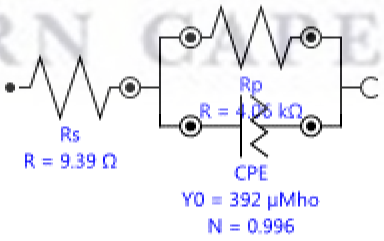


Fig. A 13; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/C commercial electrocatalyst

APPENDIX A14; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on binary PtRu/MWCNT electrocatalyst produced by impregnation method.





ptru

impregnation

Fig. A14; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRu/MWCNT electrocatalyst produced by impregnaion method.

APPENDIX A15; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on ternary PtRuW/MWCNT electrocatalyst

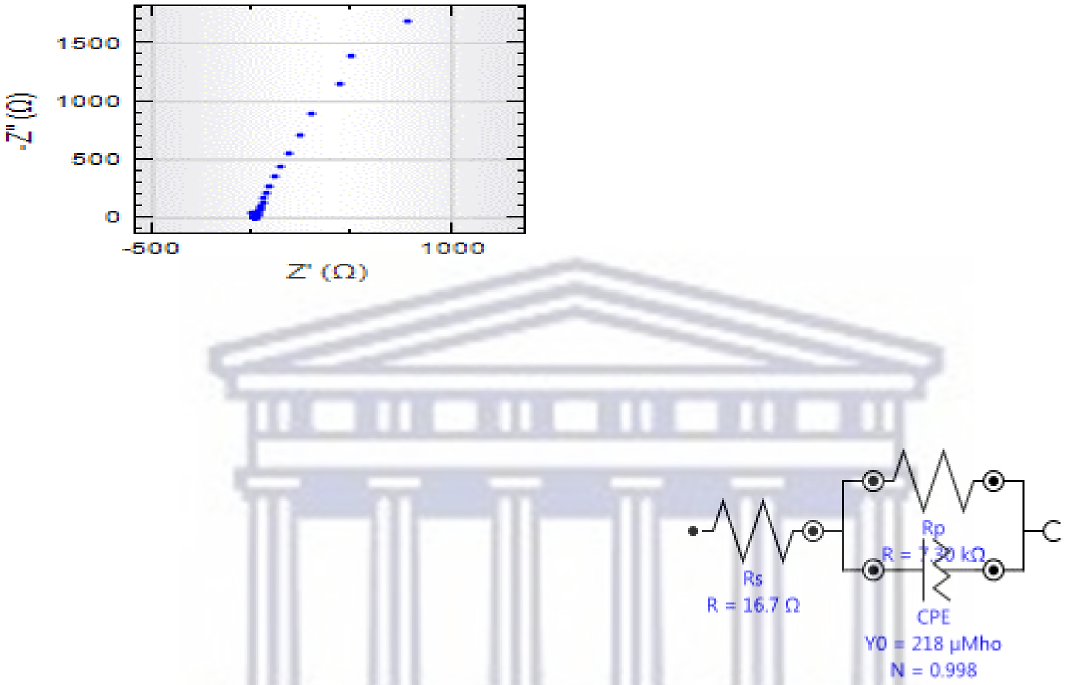


Fig. A 15. ; Nyquist plot and Equivalent circuit for the electrochemical impedance spectroscopy of methanol oxidation on PtRuW/MWCNT electrocatalyst