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ELECTRO-CATALYTIC PROPERTIES OF PALLADIUM ALLOY CARBON NANOFIBER COMPOSITE MATERIALS AS ELECTRODE IN DIRECT ALCOHOL FUEL CELLS

by

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Dissertation in fulfilment of the requirement for the degree

MASTER OF TECHNOLOGY

in

CHEMISTRY

in the

FACULTY OF SCIENCE

of the

UNIVERSITY OF JOHANNESBURG

Supervisor: Dr N.W Maxakato
Co-supervisor: Dr A.S Adekunle
DECLARATION

I hereby declare that this dissertation, which I herewith submit for the research qualification

MASTER OF TECHNOLOGY DEGREE IN CHEMISTRY

to the University of Johannesburg, Department of Applied Chemistry, is, apart from the recognised assistance of my supervisors, my own work and has not previously been submitted by me to another institution to obtain a research diploma or degree.

________________________________________ on this 30th day of November 2018
(Candidate)

________________________________________ on this 30th day of November 2018
(Supervisor)

________________________________________ on this 30th day of November 2018
(Co-supervisor)
The research work is dedicated to God Almighty for his protection and guidance throughout my master's studies and to my wonderful family.
ACKNOWLEDGEMENTS

This thesis represents the culmination of my research carried out between February 2017 and November 2018 at the Department of Applied Chemistry at University of Johannesburg. I would like to acknowledge several individuals for their contribution, support, guidance, and assistance throughout this period.

▪ First and foremost, I would love to thank God Almighty for blessing and keeping me till this far.

▪ I would love to thank my supervisors, Dr N.W Maxakato, Dr A.S Adekunle for their guidance and for the very high standard they set, which pushed me to be better than I was.

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PRESENTATIONS AND PUBLICATIONS

Conference Presentations:


Publications:


Award:

- 2nd Best Poster Presentation, 3rd Postgraduate Research Symposium in conjunction with the 8th Eskom TESP Seminar Series, University of Johannesburg, Doornfontein, South Africa, 11-12 September 2018.
ABSTRACT

Highly-dispersed palladium-based electro-catalysts on a conductive carbon support are ordinarily utilized as anode materials in low-temperature direct alcohol fuel cells. The activity and stability of these electro-catalysts firmly rely upon the attributes of the carbon support material. This study focused on monometallic Pd and binary Pd-Ru electro-catalysts supported on functionalized carbon nanofibers using alcohol reduction method. Carbon nanofibers (CNFs) were successfully prepared employing a chemical vapor deposition method using chicken oil as a starting material. The unique worm-like morphology made the material very interesting as carbon support for fuel cell electro-catalysts.

The synthesized nanomaterials were studied using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Transmission electron microscopy (TEM), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). The FTIR results confirmed that the prepared carbon nanofibers are functionalized with carboxylic acid functional groups which facilitate the dispersion of metal nanoparticles. The Raman spectrum revealed that the synthesized CNFs contains two peaks D and G bands, which correspond to a disordered carbon peak (D) and graphite peak (G). The morphology, shape and particle distribution were confirmed using TEM. The micrographs showed that Pd and Pd-Ru nanoparticles were successfully attached onto the functionalized carbon nanofibers. The metal loading and the presence of Pd, Ru, C and O elements for the synthesized electro-catalyst was examined using SEM/EDS. XRD peaks confirmed that the carbon nanofibers were amorphous and Pd (111), (200), (220) and (222) facets were observed on the surface layers of Pd/CNFs and Pd-Ru/CNFs electro-catalysts. XPS results showed the composition of the prepared samples and oxidation states of Pd and Ru of the synthesized electro-catalysts.

The electro-catalytic behavior of the Pd/CNFs catalyst was tested towards the ethanol and methanol electro-oxidation in alkaline media to assess the performance of the CNFs support material against the commercial Pd/C electro-catalyst. Cyclic voltammetry (CV) and chronoamperometry (CA) results showed that the Pd/CNFs electro-catalyst prepared by alcohol reduction method exhibit superior performance as compared to the commercial Pd/C electro-catalyst for both ethanol and methanol electro-oxidation in alkaline media.
The detailed electrochemical investigations (including CV, CA and EIS) showed that Pd-Ru/CNFs electro-catalyst has better catalytic activity, with high current density, better long-term stability and high poisoning tolerance as compared to Pd/CNFs and commercial Pd/C electro-catalyst. These results confirm that the addition of Ru nanoparticles to Pd/CNFs composite material improved the electro-catalytic activity by increasing resistance towards the poisoning of the Pd catalyst surface by strongly carbonaceous intermediate material. The results also revealed that catalytic electro-oxidation of ethanol and methanol at Pd-Ru/CNFs electro-catalyst on GC electrode platform was more conductive, with faster electron transfer kinetics at lower potentials compared to Pd/CNFs and commercial Pd/C electro-catalysts. The observed results also proved that the introduction of Ru nanoparticles to the Pd/CNFs composite material decreased the charge transfer resistance ($R_{ct}$) significantly, and hence enhances the rate for heterogeneous electron transfer kinetic process.

**Keywords:** carbon nanofibers; electro-catalysts; direct alcohol fuel cells; cyclic voltammetry; chronoamperometry; impedance spectroscopy; methanol; ethanol; palladium and ruthenium.
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<td>DAFC</td>
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CHAPTER 1
INTRODUCTION

1.1. Background of the study

Environmental problems and the growing global demands for energy have inspired intensive researches to identify new sources of clean and substitute non-sustainable power sources for fossil fuels, for example, oil and coal [1-3]. Development of alternative environmentally friendly energy sources such as biomass that will not lead to the atmospheric air pollution that is caused by anthropogenic greenhouse gas emissions due to burning of fossil fuels is of great need. High efficiency improvement of end-use equipment can be done by combining energy sources with fuel cell conversion system for future power generation.

Fuel cell technology appears to be the most promising solutions for creating power through converting chemical energy potential to electrical energy [4-6]. The main advantage of fuel cells is their higher effectiveness compared to the non-renewable fossil fuels. Fuel cell as green energy device emits zero contaminant since it operates on pure hydrogen that is less dangerous to store and transport.

The performance of the DAFCs depends on the principle and mechanisms of the electrochemical oxidation of alcohol and the reduction of oxygen. The interest is greater in direct alcohol fuel cells because the utilization of liquid fuels streamlines the fuel conveyance system, contrasted with hydrogen-fed fuel cells [5,7]. DAFCs are the most advanced candidates for stationary applications, power sources for transportation and portable electronics [8-9]. It is critical that the fuels employed in the electro-oxidation process do not degenerate the electrode catalysts. For fuel cell technology to be a competitive source of power, the fuel sources should be promptly accessible, sustainable and inexpensive. Ethanol converted from biomass as derived fuel stocks produces less atmospheric pollutants and can be used in the direct ethanol fuel cells to generate electricity in both the close and prolonged future [10-12].

The less expensive palladium catalysts have been studied and shown to show higher activities and poisoning resistances for electro-oxidation of ethanol
Chapter 1: Introduction.

compared with platinum catalysts in alkaline media. Furthermore, the alloying of palladium with different metals as co-catalysts enhances its activity, stability and toxic substance resilience [13]. For getting good catalysts one may pay attention to the morphology, shape, dispersion and to the support material. The support material is normally established via carbon matrix, recently utilized in a lot of nanostructures (tubes, wires, fibers etc.). The low cost and availability make the carbon nanofibers (CNFs) material the most used support for electro-catalysts in low temperature fuel cells. CNFs have been generally studied as a flexible catalyst support, with great electrical, thermal conductivity and high strength/solidity in the fuel cell [14].

1.2. Problem Statement.

Energy concerns and environmental pollution caused by economic and population growth are becoming a challenge all over the world [15]. During the previous years, methanol as a fuel in direct methanol fuel cells has played a tremendous critical role as an electricity source for compact gadgets because of high specific energy density, high energy transformation efficiency of 40-50%, and the utilization of methanol as a fuel allows for easy storage and transportation [16-18]. However, they suffer from limitation such as volatility, toxicity, methanol crossover from the anode to the cathode side and it reduces the cathode potential which results in low kinetic of the fuel cell as well as the wastage of fuel, in this way it is not considered as a favourable and well-disposed fuel [19-20]. Furthermore, methanol oxidation reactions lead to the poisoning of the platinum electrode due to the formation of carbon monoxide as a by-product during the methanol dissociation process which blocks the active site of the platinum catalyst, resulting in low alcohol oxidation kinetics hence low current density production [16-18]. Moreover, the high cost of the platinum electro-catalyst is the problem in fuel cell technology and has been identified as the key challenges that are inhibiting the full commercialisation of DAFCs [21]. Therefore, this study attempts to develop catalysts to alleviate the problem of the high cost of the anode catalyst materials and improve the CO poisoning resistance of the Pt catalyst.
1.3. **Hypothesis**

In this research work, the hypothesis investigated is that the particle size, shape and morphology of Pd and Pd-Ru electro-catalyst supported on carbon nanofibers (CNFs) and the synthetic method needed to make the catalysts will affect the electro-catalytic activity of the monometallic and bimetallic palladium nanoparticles. In adding platinum group metal such as ruthenium (Ru) to Palladium (Pd), non-traditional structures may be formed arising from the different metal mixing process. Mono and binary palladium-based catalysts will be evaluated for their catalytic activity towards oxidation of ethanol and methanol fuels. It is expected that using a carbon support material such as carbon nanofibers with large surface area, oxygen-containing functional groups, and high porosity will enhance palladium utilisation and improve electrocatalytic activity. The benefits of employing palladium as a primary metal, ruthenium or nickel as the second metal, carbon nanofiber as support material and ethanol or methanol as a fuel can only be realized if oxidation proceeds completely to CO$_2$ and the reaction by-products are minimized.

After synthesizing, characterizing and establishing that these electro-catalysts are capable of oxidizing liquid fuels such as methanol and ethanol, a hybrid anode will be constructed that combines the efficient oxidation properties of metal catalysts that are able to oxidize reaction intermediates for improved anode performance. This work also aims at synthesising highly functionalized carbon nanofibers using nontoxic chemicals and environmentally friendly solvent.

1.4. **Aim and objectives**

The aim of the study was to develop an alternative active electro-catalyst for direct alcohol fuel cells with anti-poisoning properties.

1.4.1. **Specific objectives**

This research project was undertaken with the following specific objectives:

- To synthesize carbon nanofibers (CNFs).
- To prepare palladium based electro-catalysts (Pd/CNFs and Pd-Ru/CNFs).
• To characterize the synthesized electro-catalysts using different characterization techniques such as HRTEM, FTIR, Raman, XRD and XPS.
• To modify and characterize selected electrode materials with the synthesized nano-materials and palladium based nano-catalysts.
• To investigate heterogeneous electron transfer kinetics of fuel cell alcohols under alkaline conditions using electrochemical techniques.

1.5. Frame-work of the investigation

Carbon nanofibers were synthesized by chemical vapour deposition method using chicken oil as a starting material catalysed with ferrocene at 600 °C for 2 hours and were functionalized using hydrogen peroxide treatment. Pd and Pd-Ru electro-catalysts were prepared using the modified alcohol reduction method and deposited on carbon nanofibers (CNFs) support material. The synthesized palladium-based electro-catalysts and commercial palladium in activated carbon were then physically and chemically characterized using different techniques as mentioned above. The commercial Pd/C was bench-marked and compared to the prepared palladium electro-catalysts for electrochemical studies.

1.6. Thesis outline

Chapter 1: Contains the background of the study, problem statement, hypothesis, framework work of the investigation, research aim and objectives.

Chapter 2: Literature is reviewed in this chapter and the focus is on the long history of fuel cells, types, advantages and disadvantages, applications, overview of electro-catalysts, previously research studies, support materials and preparation methods of electro-catalysts.

Chapter 3: Discusses the methods used in this study. This chapter also outlines the different characterization techniques for synthesized materials.

Chapter 4: The results and discussion of the synthesised palladium nanoparticles supported on carbon nanofibers (Pd/CNFs) are presented and discussed along with the commercial Pd/C catalyst. Chapter four also provides information on the
physical and electrical properties of the CNFs supported electro-catalyst for ethanol and methanol oxidation reactions (EOR and MOR) in alkaline medium.

**Chapter 5:** The results and discussion of Pd-Ru/CNFs electro-catalyst on glassy carbon electrode are presented and discussed along with commercial Pd/C for EOR and MOR in alkaline medium.

Finally, **Chapter 6** provides key conclusions found in the previous result chapters as well as fundamentals and the behaviour of the synthesised electro-catalysts under different conditions investigated. The chapter also list some recommendations made from the study.

**References:** are listed at the end of each chapter.

**Appendix section:** selected prominent data is presented in this section.
References


2.1. The long history of fuel cells

A fuel cell is a device in which electrochemical energy sources of a chemical reaction of a fuel stored in (e.g. Methanol, ethanol and ethylene glycol) and oxidant (hydrogen and oxygen) is directly converted into electrical energy, just like a battery [1-3]. Although, unlike batteries, which will keep pace with the accelerating power demands, fuel cells produce electricity if the reactants hydrogen and oxygen are supplied. The primary demonstration to a fuel cell can be ascribed to a scientist William Grove in 1839, using an experiment that demonstrates, water is being electrolysed into gases (hydrogen and oxygen) by passing an electric current through it. The electrolysis at platinum electrode, which were inundated in weaken sulphuric acid, is being reversed and the gases are recombined producing electrical current [4-5]. The quicker the electro-chemical reactions at the electrodes, the higher the current output of the fuel cell which make the choice of catalysts an essential foundation for fuel cell outline.

In 1882, Lord Rayleigh of British developed a new form of gas battery and improvements were done by increasing the area of contact between the gas, the
liquid electrolyte allowing the gas to diffuse to the solid electrolyte and this surface of action was increased to enhance the efficiency of the platinum electrode. Apart from using the combination of hydrogen and oxygen as a fuel, he also uses coal as the source of fuel and the produced current from the gas battery was considerable despite the poor performance. Five years later in 1887, another approach to form a new gas battery was described by Alder Wright and Thompson. This new form of gas battery was acquired by using two aeration plate cells, one is in contact with oxidizable hydrogen gas and one with the air open to the atmosphere. These researchers also develop the use of zinc or aluminium metal with a fluid, such as solution of sodium hydrosulfite or ammoniacal cuprous oxide as the sources of energy to produce powerful currents and large aeration plate cells. The highest voltage achieved was 0.6 to 0.7 volts by each cell with moderate current.

In 1896, William W. Jacques constructed a fuel cell to produce electricity by converting the energy directly from coal, but the production of electricity was complicated and inefficient. However, Haber and Bruner (1904) after seeing the demonstration of Jacques concluded that the coal was chemically reacted with the alkaline electrolyte and then with the iron electrode instead of the direct oxidation coal fuel cell. The improvements of the theory were made by Haber and Bruner substituting the iron with platinum electrode and it worked. Baur and Ehrenberg (in 1912) reported many experiments on high temperature fuel cells. Their work research was including investigation of suitable electrolyte among soda, potash, carbonate, cryolite and borate after selecting a good molten silver as the cathode. In 1930s, Oganes Davtyan of the Union republics investigated electrolytes with conductors at high operating temperatures and low operating temperature alkaline fuel cells. He develops a solid electrolyte and increase the conductivity to obtain a stable electrolyte for highly efficient power supplier in fuel cell technology. Davtyan’s research studies in molten carbonate and solid oxide fuel cells were published in 1947 [7-8]. British engineer Francis Thomas Bacon in 1932 constructed the new successful gas battery running on pure oxygen and hydrogen by improving the one designed by Mond and Langer. His modification was based
on using potassium hydroxide as an alkali electrolyte and nickel as electrodes [9-10].

Fuel cell developments can be traced back to 1950s when W. Thomas Grubb and Leonard Niedrach, were jointly designing proton exchange membrane fuel cell by using a sulphonated polystyrene as polymer electrolyte and this scientist were working for the General Electric Company. After inventing the polymer electrolyte membrane in 1955, five years later Grubb and Niedrach’s develops electrochemical hydrogen oxidation and oxygen reduction reaction where platinum was deposited on to the membrane, which served as catalyst at temperature below 150 °C. GE researchers partnered with the National Aeronautics and Space Administration (NASA) and McDonnell Aircraft jointly develop the technology prompting its utilization amid Project Gemini. This was the primary commercial utilization of a fuel cell [11].

2.2. Basic Operation of Fuel Cells

Generally, a fuel cell comprises of an electrolyte sandwiched between anode and cathode which vary depending on the system. A fuel (usually a hydrogen rich fuel such as methanol and ethanol etc) is oxidized at the anode where a catalyst generating separates negatively charged electrons and positively charged ions. The electrons from the anode side move through an outside electrical circuit to the positively charged cathode, the positively charged ions must travel through the electrolyte to reach the cathode side, finishing the circuit (Figure 2.2). This motion of electrons is an electrical current. At the cathode, oxygen consolidates with electrons and ions producing water or hydroxide ions [12-13].
2.3. Types of fuel cells

There are six distinct sorts of fuel cells and are fundamentally partitioned by the electrolyte they utilize and working temperature. Low temperature fuel cells are categorized into four types, the Alkaline Fuel Cell (AFC), the Direct Alcohol Fuel Cell (DAFC), the Phosphoric Acid Fuel Cell (PAFC), and the Proton Exchange Membrane Fuel Cell (PEMFC). The high temperature fuel cells are classed into two types, the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). An overview of the six distinct sorts of fuel cell is given in Figure 2.3.
2.3.1. **Proton exchange membrane fuel cell (PEMFC)**

This is a very common type of fuel cell that utilizes a polymer membrane as the electrolyte which isolates the anode and cathode electrode. PEMFC are typically fuelled with liquid hydrogen and the platinum catalyst is used for both anode and cathode at low temperatures. This fuel cells work at temperatures beneath 100°C which permits fast start-up. High cost of platinum catalyst and low operating efficiency (40-50%) are major problems of PEMFC. The advantages of PEMFC are its small weight and volume contrasted to other types of fuel cells [16–18]. This polymer electrolyte membrane has a high-power density characteristic that makes them a good candidate for portable applications and their rapid start up qualities for automotive vehicles.

**Figure 2.3:** Types of Fuel Cells. Anode and cathode reaction, charge carrier in the electrolyte, operating temperature are presented [15].
2.3.2. Alkaline fuel cell (AFC)

This is one of the developed fuel cell systems used by NASA to power the Apollo series emissions on spacecraft. AFC mainly use aqueous solution of potassium hydroxide in water as the electrolyte and work at lower temperatures ranging between room temperature to 90 °C in KOH solutions [19]. One of the advantages of AFC is its higher performance, cathode reaction kinetics are substantially quicker in alkaline electrolyte than in acidic electrolyte. Moreover, low cost of the used catalyst such as nickel and electrolyte such as potassium hydroxide is another advantage of alkaline fuel cell [20-21]. The major disadvantage of AFC is it is easily poisoned by carbon dioxide and it requires pure hydrogen and oxygen to be sustained into the fuel cell [22].

2.3.3. Phosphoric acid fuel cell (PAFC)

These are the fuel cell type that utilizes concentrated phosphoric acid as an electrolyte that is contained in a silicon carbide structure pasted into a Teflon gasket [23]. PAFC employ platinum catalyst dispersed on carbon material as the electrodes for both anode and cathode. The medium operating temperature of the PAFC is in the range between 100 – 250 °C [24]. The main advantages of this kind of fuel cell is the co-generation of electricity with high power efficiency around 80 percent. PAFCs are carbon dioxide tolerant with a concentration of 1.5 % which broadens the number of fuels that can be utilized. The major drawbacks of PAFCs is the use of expensive platinum as a catalyst which expands the expense of the fuel cell and they are large and very heavy [25]. This kind of fuel cell system is used to generate electric power for large stationary applications and huge vehicles such buses.

2.3.4. Molten carbonate fuel cell (MCFC)

This is a high temperature fuel cell that utilizes alkali metal solutions of sodium carbonate or potassium carbonate salt suspended in a matrix as an electrolyte [26]. MCFCs operate at high temperatures typically ranging from 620 to 660 °C and lithium aluminium oxide is used as a bimetallic catalyst in both electrodes, reducing cost [27]. These fuel cells are flexible they can operate using different types of fuels, cheaper metal catalysts and they have high efficiency from 50% up
to 60% due to high operating temperatures. MCFCs has the potential to be fuelled by hydrogen, carbon monoxide, methane, natural gas, landfill gas and coal gasification products for electrical utility and large industrial power applications [28]. The primary disadvantage of MCFCs is the intolerance to sulfur and the carbonate electrolyte produces carbon dioxide which causes the anode and cathode corrosion problems.

2.3.5. **Solid oxide fuel cell (SOFC)**

This works at very high temperatures (800 to 1000 °C) and it uses a hard-non-porous ceramic electrolyte such as yttria-stabilized zirconia material [29–30]. In SOFC negative ions travel through the electrolyte to the anode to join with hydrogen to generate water and electrons. The high operating temperatures removes the need for precious-metal that can be utilized as electro-catalyst at the anode and cathode, hence lessening the expense in Solid oxide fuel cell. Because SOFCs operate at high temperature, natural gas is converted directly to hydrogen rich fuel by the process called internal reforming using heat from the fuel cell. Thermal energy and water by-products can be reused and recycled in the fuel processor to produce electricity or enhance energy efficiency with co-generation [31]. The main advantages of SOFCs is the high power-generating efficiency around 60% for stationary applications and for auxiliary power units used in electric vehicles [32].

2.3.6. **Direct Alcohol Fuel Cells (DAFC)**

The DAFCs is a promising green energy device which produces electricity by direct electrochemical oxidation of small molecules of alcohol as the fuel [33]. Due to low cost, simple handling, storage and high energy density, direct ethanol fuel cells (DEFCs) and direct methanol fuel cells (DMFCs) are the most popular types of fuel cells among DAFCs. The performance of a DAFC depends on the catalyst activity and lifetime. The DAFC system contains Membrane Electrode Assemblies (MEAs) constituted by anode, polymeric electrolyte membrane and cathode mechanically pressed onto each other. In general, the DAFCs cannot operate at temperatures higher than 120 °C due to the low thermal stability of the membrane. The detriment with DAFC is that the electrolyte could become carbonated by CO₂ impurities in the oxygen source – which is the reason alcohol electro-oxidation
studies have been done basically in KOH and NaOH [34]. Carbonation diminishes electrolyte conductivity, oxygen solvency and electrode efficiency and can likewise hinder the pores of the electrode [35]. Therefore, KOH is favored than NaOH because of its higher ionic conductivity and higher solvency product of $K_2CO_3$ [36].

2.3.6.1. Advantages of Direct Alcohol Fuel Cell in alkaline medium: [37]

- The ability to use both noble and none-noble metals to prepare electro-catalyst.
- Enhanced kinetics at both electrodes with low over potential values at the anode during alcohol oxidation.
- Minimal alcohol crossover from the anode to the cathode side due to electro-osmotic drag of the hydrate hydroxyl ions.
- Easier water management
- Lower susceptibility of the materials towards corrosion due to the alkaline environment.

2.3.7. Principles and Mechanisms of a Direct Methanol Fuel Cell (DMFC)

The Direct Methanol Fuel Cell (DMFC) is one of the most form of low-temperature fuel cells that uses liquid hydrocarbon such as methanol, water and air to produce electricity from electrochemical reactions without using combustion engines [38]. Methanol is the least complex organic alcohol that is more reactive in alkaline solutions and it has no C-C bond that is hard to divide at low temperatures. DMFC employ potassium hydroxide or sodium hydroxide as the electrolyte material. Contrasted with the utilization of hydrogen in fuel cells, fluid alcohol fuels are uncomplicated to store and transport. The direct oxidation of alcohol will likewise dispose of an overwhelming reformer expected to produce hydrogen from fluid or gas carbonaceous fuels. Figure 2.4 demonstrates a schematic diagram of a direct methanol fuel cell in alkaline media with a blend of sodium hydroxide, methanol and water flowing in the anode and oxygen in the cathode.

On the anode, methanol is oxidized to carbon dioxide and electrons are generated, while on the cathode side, oxygen receives electrons and is reduced to generate hydroxide ions. The hydroxide ions travel through the electrolyte to the
anode. The chemical reactions and standard hydrogen electrode (SHE) [vs. thermodynamic potential] on every cathode and anode are demonstrated as follows:

Anode oxidation:

\[
\text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow 6\text{e}^- + \text{CO}_2 + 5\text{H}_2\text{O} \quad E^\circ = -0.81 \text{ V} \quad (2.3.1)
\]

Cathode reduction:

\[
\frac{3}{2}\text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow 6\text{OH}^- \quad E^\circ = 0.40 \text{ V} \quad (2.3.2)
\]

Overall reaction:

\[
\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad E^\circ = 1.21 \text{ V} \quad (2.3.3)
\]

Figure 2.4: Schematic principle of direct methanol fuel cell in alkaline media.

2.3.7.1. Below are some of the Challenges Facing the Commercialization of DMFC: [39]

- Low electro-catalyst activity.
• The inability of the anode electro-catalyst to resist poisoning from strongly adsorbed intermediates that are formed during the electro-oxidation reaction of methanol.

• Methanol crossover from the anode to cathode through the nafion type membrane.

2.3.8. Mechanisms and Principles of a Direct Ethanol Fuel Cell (DEFC)

The DEFC is the most suitable alternative candidate of low temperature fuel cell which utilizes a membrane to isolate the chemical reduction and oxidation reaction to produce an electrical current. Ethanol is an interesting fuel for DAFCs because of numerous advantages for example, high energy density and low toxicity compared to methanol. Ethanol can be effectively created from sustainable sources by fermentation process of agricultural biomasses. DEFC are named for the membrane that isolates the cathode from the anode. The membrane electrode assembly consist of Diffusion Layer (DL), Catalyst Layer (CL), Anion Electrode Membrane (AEM) and their function is to allow hydroxyl ions from the anode to the cathode. A typical DEFC is shown in Figure 2.5:

The oxidation reaction of ethanol from the anode side and the reduction reaction of oxygen from the cathode side can be shown by means of equations. On the anode ethanol is oxidized to produce carbon dioxide, water, and electrons as indicated by Eq. (2.4.1),

\[ \text{CH}_3\text{CH}_2\text{OH} +12\text{OH}^- \rightarrow 2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \]  \hspace{1cm} (2.4.1)

From the ethanol oxidation reaction, the produced water in ethanol solution diffuses through the membrane to the cathode catalyst layer. The entire electro-oxidation of ethanol to carbon dioxide incorporates 12 electrons which passes through an outside circuit to the cathode. In cathodic oxygen reduction reaction, the oxygen combines with water from the anode to generate hydroxide ions which are flowing through the cathode dispersal layer to the cathode catalyst layer as indicated by Eq (2.4.2):

\[ 3\text{O}_2 + 6\text{H}_2\text{O}+12\text{e}^- \rightarrow 12\text{OH}^- \]  \hspace{1cm} (2.4.2)
The entire ethanol oxidation reaction indicated by Eq. (2.4.1) isn't accomplished. The primary product of the reaction is acetate ion preferably than carbon dioxide as following:

\[ \text{CH}_3\text{CH}_2\text{OH} + 5\text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} + 4\text{e}^- \]  

(2.4.3)

Overall reaction of DEFC in the alkaline media is:

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 + \text{OH}^- \rightarrow 2\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \text{ (anionic membrane)} \]  

(2.4.4)

**Figure 2.5:** Schematic principle of direct ethanol fuel cell in alkaline media [40].

### 2.4. Applications of fuel cells

**Table 2.1:** Type of fuel cells and their applications.

<table>
<thead>
<tr>
<th>Application Type</th>
<th>Stationary</th>
<th>Electric Vehicle</th>
<th>Portable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Power Range</td>
<td>0.5 kW ~ 400 kW</td>
<td>1 kW ~ 100 kW</td>
<td>5 W ~ 20 kW</td>
</tr>
<tr>
<td>Typical Technology</td>
<td>DAFC, PEMFC, MCFC, PAFC</td>
<td>DAFC, PEMFC, AFC</td>
<td>DAFC, PEMFC</td>
</tr>
</tbody>
</table>
2.4.1. Stationary Power

The stationary power systems for fuel cell technology generates heat and electricity to power hospitals, residential flats, industrial facilities and small villages where no electricity is available. There are a wide range of uses of fuel cells being used right now such as power sources for spacecraft, remote weather stations, and military applications. Stationary power fuel cells are highly reliable and long lasting compared to conventional electric generators used to power hospitals, houses and businesses [41].

2.4.2. Transportation Power

Transport fuel cells produces electricity as a power source for vehicles such as cars, trucks, buses and submarines. Electric vehicles powered by hydrogen-oxygen fuel cell emit zero emission and they have higher efficiency than vehicles powered by batteries [42]. This power technology motivated several major car companies including Daimler-Chrysler, Ford, Nissan, Mazda, Toyota, Honda and Hyundai to start building vehicles using fuel cells with pure (gaseous or liquid) hydrogen because they see potential in this new form of technology compare to conventional internal combustion engines.

2.4.3. Portable Power

Portable fuel cell framework can be utilised to power electronic gadgets for example laptops, cell phones, camcorders and other low-power appliances. Low working temperatures are necessary and fuel cells with power densities from 25 W to 5 kW are utilized in portable electronic devices. Small hydrogen fuel cells can be utilized to produce electricity to telecommunications satellites by supplanting solar panels. Finally, proton exchange membrane fuel cells can be utilized to power for biological applications, such as wireless hearing aids and cardioverter defibrillators [43].
2.5. Advantages and disadvantages of Fuel Cells

2.5.1 Low or zero greenhouse emission

Fuel cell systems at lower temperatures emit zero emissions when running on direct pure hydrogen and air generating only electricity, water and heat as by-product. The use of low temperatures fuel cells circumvents electrochemical reactions involving contamination by nitrogen oxides, sulphur oxides and carbon dioxide for kilowatt of power generated [44-45]. Even fuel cells that employ hydrogen-rich reformate gas mixtures as a source of fuel, the emission produced from these sources is still lower than conventional internal combustion engines or batteries.

2.5.2. High efficiency

Fuel cell systems have high energy proficiency when contrasted to heat engines as they are not restricted by the Carnot cycle efficiency at low operating temperatures. The higher efficiency of fuel cells isn't administered by thermodynamic efficiency laws such as the Carnot thermic cycle. Fuel cells converts energy of chemical reaction of a fuel into electrical energy without the combustion process. Fuel cells systems can provide higher fuel to electricity using liquid hydrocarbon fuels such as natural gas [46].

2.5.3. Modularity

Fuel cells are modular in construction and connected in series or in parallel to produce higher voltages. Unlike batteries, fuel cells are used for large scale applications which ranges from 1W, kW up to MW and they exhibit higher efficiency regardless of the size. Cell stacks consist of several elementary units, each comprise of an anode, cathode, electrolyte and a bipolar separator plate [46-47].

2.5.4. Low Maintenance

Due to high modularity of fuel cell systems, more simple construction, high reliability and lower maintenance costs [48-50].
2.5.5. **Silence**
Fuel cells produce weak noise and vibration since they have no mobile parts except for the pumps and transformers.

2.5.6. **Flexibility**
Fuel flexibility depends upon the sort of fuel cell and the operating temperature utilized. For low temperature fuel cells, pure gases are required to operate; the higher the temperature, the less pure gases are required [48].

2.5.7. **Disadvantages of fuel cells**

2.5.7.1. **High costs**
Due to the high value of components, fuel cell costs for stationary amalgated heat and power systems are still too high compared with available fossil fuel technologies. The cost for stationary electric systems is US$1000 per kW and an operation life cycle of 40,000 hours is required [50–51]. For transportation applications, a cost of US$10 to $50 per kW and a primary operation lifetime of 4000 hours is required. These high costs of electric vehicles are due to heavy fuel cell systems (weight and size) and use of an expensive platinum catalyst to elevate the electrical generation reaction but still they are greater than internal combustion engine technology. For large power plants, the cost of a fuel cell system is around US$3000 per kW with extra expenses of thermal management, for the large amount of heat exchange with an operative cooling system and this high cost, weight and size concurrently decrease the lifetime of a fuel cells [52–53].

2.5.7.2. **Storage**
The use of expensive hydrogen as a fuel in low temperature fuel cell technologies is a significant challenge because it is difficult to manufacture and store in large amounts of volumes. At cryogenic temperatures, fuel cells employ pure hydrocarbon or alcohol fuel not contaminants such as sulphur and carbon compounds that will deactivate or destroy fuel cell catalyst [44].
2.5.7.3. Stability issues

The length of life time of fuel cell technologies is still very low at high temperature especially for automotive applications. It is 4000 hours and 40,000 hours for stationary applications [54].

2.6. ELECTROCATALYSIS and ELECTROCATALYSTS

2.6.1. Overview of Electro-catalysts

In 1963 Grubb, reported the investigations of fuel cells and he suggested the use of the term "electro-catalysis" however the primary interpretation was done earlier than in a well-known paper by Horiiuti and Polanyi [55-56]. Electro-catalysis: past, present and future. Electro-catalysis is a type of catalysis where electrochemical reactions are being catalysed to accelerate the rate of reaction mechanisms at electrode surfaces [57]. The aim of putting an electrochemical reaction to the surface of the catalyst is to furnish an alternate reaction pathway with a lower activation energy of a rate limiting step [58]. Figure 2.6 shows the catalyzed pathway mechanisms including two additional steps as illustrated in the reaction diagrams. As shown in the figure below the catalyzed reaction has lower activation energy compared to un-catalyzed reaction. At lower activation energy electrochemical reactions are faster and more economical in terms of energy requirements. In catalytic reaction process there is either increment of the rate or current density of an electrode surface at stated potential and the catalysts are not consumed in the chemical reaction. Electro-catalysis consists of two chemical catalysis homogeneous and heterogeneous catalyst. In homogeneous catalysis, both the catalyst and the reactants are available in a similar phase e.g. transitional metal complexes. A heterogeneous catalyst is a catalyst that is available in a dissimilar phase (usually a solid) than the reactants. In heterogeneous catalysis, both catalysts and reactants are in different phase immobilize on the electrode surface e.g. Rhodium nanoparticles [59].
2.6.2. Catalysts for alcohol oxidation in direct alcohol fuel cell.

An electro-catalyst is a type of catalyst that can speed up the rate of an electro-chemical reaction occurring on the surface of electrode without being consumed in the process. The performance of a fuel cell system dependent on the activity of the anode and the cathode electro-catalyst [60]. The electro-catalytic activity of the catalyst depends on the support material used. The chemical nature and nanostructure of electrode material play a critical role in adsorption and electro-catalysis particularly in electrochemical oxidation of some organic fuels [39]. It is extremely important to develop electrode material which are chemically compatible with the material of the electrolyte in fuel cells [61].

Platinum metal is the most utilized anode electro-catalyst in direct alcohol fuel cell with few problems. Pt is a very expensive catalyst that is easily poisoned by strongly adsorbed oxidation intermediates and it is less abundant or scarce in the earth crust which increases the cost of potential fuel cells. For all these reasons Palladium has as of late pulled in consideration as an alternative catalyst to platinum when alloyed with non-noble metals for both DMFC and DEFC. This
metal is less expensive and 50 times more abundant compared to platinum metal on earth [62-63]. In electro-catalysis Palladium metal is the most promising electro-catalyst for alcohol fuel electro-oxidation showing better tolerance to the CO-containing intermediates [64]. The Electrochemical oxidation of alcohol fuel is kinetically favourable which can be effectively catalysed by palladium in alkaline solutions [3-37]. Pd electro-catalyst show high catalytic activity towards EOR than Pt electro-catalyst in alkaline media. Unlike the methanol oxidation reaction, EOR is incompletely oxidised producing intermediates and by-products such as acetate, this is significantly decreasing the overall fuel cell performance.

The problem of the slow alcohol oxidation rate has been reduced to some extent by alloying Pd with non-precious metal such as Ru, Sn, Mo and Cr etc. [65]. It is believed that the electro-catalytic activity of the catalyst can be enhanced by alloying a second or third transition metal when developing the electro-catalyst to form a binary or a ternary electro-catalyst [4].

2.6.3. Previously Reported Performances of anode catalysts in DAFC.

Hu et al. have studied the oxidation of ethanol on Pd/C and The Pd-WC/MWCNT electro-catalysts in alkaline medium by preparing Pd NPs promoted with WC supported on MWCNTs by an intermittent microwave heating (IMH) technique. The electro-catalysts demonstrated better EOR performance in (1 M KOH + 1 M C₂H₅OH). The same group synthesized Pd NPs promoted with NiO supported on activated carbon by the intermittent microwave heating (IMH). The Pd-NiO/C catalyst demonstrated highly improved kinetics for oxidation of ethanol in alkaline solution [67-68].

Amin et al. investigated Pd and Ni oxides/hydroxide supported on carbon black (Pd-Ni/C) electro-catalyst towards methanol oxidation by determining the surface coverage of Ni in these composites, attempting to correlate the existence of Ni oxides and hydroxides with the MOR current densities. Pd-Ni electro-catalysts have high catalytic activity as compared to monometallic Pd because Ni is oxophilic like Ru, which has the ability to produce adsorbed Ni hydroxides at a lower potential and facilitates the oxidation of the carbonaceous intermediate material.
Moreover, the surface Pd-Ni composites and NiO or NiOOH species can improve the adsorption capacity towards ethanol by producing a surface oxygen containing species that binds with carbon monoxide at lower potential [69].

Bambagionia et al. have deposited Pd particles spontaneously on MWCNTs by the impregnation-reduction method towards ethanol, methanol and glycerol oxidation reactions in alkaline conditions. The Pd/MWCNTs electro-catalyst have high catalytic activity for alcohol reduction reactions in (2 M KOH) alkaline conditions. However, this electro-catalyst is chemically stable only for the ethanol oxidation reaction. Methanol and glycerol oxidations lead to the development of carbon monoxide which can possibly contaminate the electrode. Ethanol is specifically oxidized to acetic acid which before long gets changed into acetate ion [70-71].

Fang et al. investigated the reaction mechanism of ethanol electro oxidation on a palladium electro-catalyst in alkaline media with different concentrations of NaOH (0.01 to 5 M). Fourier Transform Infrared (FTIR) and cyclic voltammetry were utilized to explore oxidation products at various pH values. They found that the ethanol oxidation activity on Pd electro-catalyst was to a great extent influenced by pH. The superior performance was obtained in 1 M NaOH. The FTIR spectroscopic estimations indicated sodium acetate as the principle oxidation product at sodium hydroxide concentration greater than 0.5 M. The dissociation of ethanol molecule occurred at pH 13 [72].

Zhang et al. acquired nanocomposite materials of palladium and vanadium oxide nanotubes (VOx-NTs) and of Pd supported on activated carbon (C) for use as electro-catalysts for the ethanol and methanol oxidation reactions in alkaline media through a basic reductive process. Results have shown that the electro-catalyst display superb activities and great stability under alkaline media [73].

Chu et al. obtained nanocomposites of Pd, In$_2$O$_3$ nanotubes and C and exhibited that the electro-catalysts by utilizing chemical reduction and hydrothermal reaction process were much better than that of Pd/CNT in regard of electro-catalysis of the ethanol oxidation reaction (EOR) in alkaline condition. The catalytic activity for the Pd-In$_2$O$_3$/CNTs composite catalysts towards the EOR is improved by alloying Pd with In$_2$O$_3$ nanotubes [74].
Bagchi and Bhattacharya studied the ethanol oxidation reaction on Pd-Ru electro-catalyst in 1 M KOH and revealed that the electro-catalyst containing the higher amount of deposit are less influenced by carbonaceous toxic substance. These results confirm that the addition of Ru nanoparticles produces surface oxygen-containing species that bonds with the strongly carbonaceous intermediates. To improve the electro-catalytic activity further, ruthenium will be added from palladium Carbon nanofiber composite material and the structure and electro-catalytic properties of the new products will be investigated, derived in relation to MOR and EOR in 1 M KOH [75-76].

2.6.4. Support materials for electro-catalysts

Several alternative carbon-based materials are used as catalyst supports for Direct alcohol fuel cells such as carbon black (CB), carbon nanotubes (CNT), carbon nanofibers (CNF), carbon microspheres (CMSs), coinlike hollow carbons (CHCs), graphene [G], titanium oxide (TiO\textsubscript{2}) nanotubes and Tungsten carbide (WC) nanocrystals and they have been recently utilized as carbon supports for Palladium catalysts with superior activity towards ethanol oxidation reaction in alkaline media [77-80]. These support materials have high surface area to obtain fine dispersion of metal nanoparticles, good electrical properties, good corrosion resistivity and stable nanoscale metallic particles due to their graphitic nature [81]. Carbon support material play a major role on the electro-catalytic performance of the catalyst in fuel cells. Moreover, the support material is supposed to have suitable porosity to boost electrolyte flow, low cost and availability to be considered as good material for a fuel cell technology [37].

2.6.4.1. Carbon Black (CB)

Carbon black (CB) is the most commonly used support material for anode and cathode electro-catalyst applications in fuel cells [82]. It is cheap, easily available which reduces the overall cost of the fuel cell, has a large surface area to obtain high metal dispersion and is highly electronic conductive [83]. These physical and chemical properties of carbon black supported metal catalysts made them to be a popular choice in fuel cell technology. There are different types of carbon blacks, namely Vulcan XC-72R, Acetylene Black, Shawinigan Chevron, Black Pearl 2000, Ketjen Black, channel black, furnace black, lampblack or thermal black and Denka
Carbon black is usually manufactured by thermal decomposition of hydrocarbons such as natural gas or coal tar oils prepared from petroleum processing in the absence of air or flame at high temperatures ranging from 1400–1800 °C [84-85]. CB exhibit a three-dimensional network structures to form different size quantization aggregates with diameters around 250 nm crystalline primary nanoparticles [86]. The major drawback of CB is a thermo-chemical instability that reduces the electro-activity of the material and the dense structure that leads to low platinum utilisation [87]. Carbon black is very unstable under acidic conditions of DMFCs, it gets corroded resulting in disintegration or dissolution of metal catalyst layer and this decreases the overall fuel cell performance [88].

Figure 2.7: A picture of carbon Black support material [89].
2.6.4.2. Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) were first made by Iijima in 1991. CNTs have pulled a great deal of attention because of its unique physicochemical, electrical and mechanical properties [90]. These unique properties coupled with lower cost compared to carbon black make CNTs a good alternative support for fuel cell catalysts [91-92]. CNTs can be classified into two categories which is single-walled (SWCNTs) and multi-walled (MWCNTs) with diameters of nanometre sizes and lengths of about one millimetre [86]. The difference between these carbon support materials are in the number of graphene layers and the arrangement of the carbon atoms. The structure of SWCNTs consist of a cylinder made up of one rolled graphene sheets whereas MWCNTs consist of a concentric rolled set of cylinders made up of many graphene sheets that are closed at both ends [93]. SWCNTs have been reported as metallic or semiconductors with high surface area typically ranges from 400 to 900 m²/g depending on the tube and helicity. MWCNTs have been found to have a relatively higher conductivity and chemical stability due to large outer shells ranging between 200 and 400 m²/g [94-95]. MWCNTs are more conductive whereas SWCNTs have larger surface area. CNTs are chemically inert by nature, as a result metal nanoparticle have poor dispersion, large particle size, which diminishes the electro-catalytic activity and they need to be functionalized with acid to be easily dispersible in solvents [96].
2.6.4.3. Carbon nanofibers (CNFs)

The properties of carbon nanofibers (CNFs) have attracted much attention because of their large specific surface area, chemical inertness, high electrical and thermal conductivity [97–98]. CNFs consist of the carbon sheets that are perpendicular or aligned in specific directions with different structural, textural characteristics and they have larger diameters compared to CNTs which ranges from 100–500 nm [99]. CNFs have a very thin fibers or no hollow cavity and the large surface areas of approximately 80 to 200 m² g⁻¹, depending on the fiber and helicity. CNFs can be classified into three types according to their complex porous structure, and extremely long fiber length which are; herringbone, platelet, and tubular, as shown in Figure 2.9 [100]. Herringbone CNFs exhibit intermediate features of parallel and platelet types, thus providing higher catalytic activity and better durability than the other types [101]. CNFs are utilized as electro-catalyst support material in fuel cell technology, in high performance electrode for supercapacitors, in field emission source and in chemical energy storage [101-
CNF-based membrane electrode assembly (MEA) are superior to carbon black-based membrane electrode assembly as catalyst supports in PEMFCs by Li et al [102]. In addition, these studies have shown that CNFs can maintain continuous electrical conduction networks in the Nafion matrix due to high length to diameter ratio [103]. In this case CNF as, electro- catalyst support has been found to reduce platinum loading in membrane electrode assembly and this enhances its activity compared to carbon black [100]. As for CNTs, the fibre surface was slightly edged where the basal plane is exposed while only the edge planes are exposed in CNFs and these planes produces electrical anchoring sites for electro-catalysts enhancing high platinum nanoparticle dispersion. Furthermore, the authors found that platinum electro-catalyst supported on CNFs show lower poisoning rates it’s because platinum nanoparticle acquire specific crystallographic orientations when dispersed on the highly disordered graphitic nanofiber crystals Many investigations have indicated improved catalytic activity for the oxidation of methanol when utilizing CNFs as the support material for electro-catalysts in fuel cells [104-105].

There are two well-known growth methods have been developed to fabricate carbon nanofibers: chemical vapor deposition (CVD) method and electrospinning polymeric nanofibers (NFs) [106]. In CVD, CNFs are grown using hydrocarbon feedstock gases over metal catalyst particle such as Fe, Co and Ni. In electrospinning, CNFs are grown using heat treatment or the action of an external electric field called carbonization process [107]. Other methods such as arc discharge and laser ablation have also been employed to produce CNFs, but these methods are highly expensive and yield small amounts of carbon compared to CVD. Among them, thermal CVD method has been considered as effective method to synthesize carbon nanofibers at temperatures between 550 and 1000 °C [108].
2.7. Preparation Methods of Electro-catalysts

There are various methods that can be used to prepare electro-catalyst in fuel cells, which include; chemical vapor deposition, polyol (alcohol reduction) method, impregnation method, spray pyrolysis, microemulsion method, sol-gel method, precipitation method, colloidal method, hydrothermal method, Bonnemann method and aerosol assisted deposition. A good method for high performance electro-catalysts should provide a narrow nanoscale size distribution, uniform particle composition and high dispersion of the metal catalyst on the support material.

2.7.1. Chemical vapour deposition

Chemical vapour deposition method (CVD) which was utilized in this study has been found to generate high purity and high-performance solid material. The impurities that may be formed are eliminated by gas flow through the reaction chamber or using distillation technique [110]. CVD is one of the most important method for the preparation of highly active electro-catalyst in fuel cells and is normally used in semiconductors to produce thin films for electronic and optical devices [111]. This technique can also be used in synthesis of carbon nanostructure materials including: carbon nanotubes, carbon nanofibers, carbon nanodots and graphene. In this method a wide range of materials can be prepared or synthesized from deposition of metals over diamond to nitride films. The main

![Figure 2.9: Schematic diagram showing three various structures of CNFs [109].](image)
advantages of CVD method, films are regularly quite conformal, and it produces a wide variety of catalysts with very high purity [112-113].

2.7.2. Impregnation method

The impregnation method is the most commonly used method for synthesizing fuel cell electro-catalysts with tiny particles typically ranges from 3 to 7 nm with controlled loading [94, 114]. Usually the impregnation method includes the following three common steps: (1) contacting the support material with the impregnating metal salt solution for a certain period and reducing metal ions to their metallic nanoparticles using NaBH₄, Na₂S₂O₃, N₂H₄, H-CHO or Na₄S₂O₅ as a reductive agent, (2) the support solid is then drained and dried to remove the imbibed liquid and (3) the metallic catalyst precursors such as H₂PtCl₆ and RuCl₃ are activated by calcination, electrochemical reduction in a liquid phase or gas phase [115-117]. The major drawback of the impregnation method is the poorer distribution of the chloride precursors that might lead to chloride poisoning, resulting in ultra-low catalytic performance and instability of the electro-catalyst [94, 114].

2.7.3. Polyol Method

Polyol method is often also called alcohol reduction method. It is a robust strategy for the synthesis of Supported nanoparticle catalysts using polymeric capping agent as a stabilizer for growth and aggregation of metal catalysts at an elevated temperature. In 1989 Fievet et al. developed the alcohol reduction method to prepare well-defined metal salts such as Co, Ni, Cu particles in terms of size, shape, composition, and crystallinity in the range of 2-7 nm with controlled loading [118]. It consists of a liquid phase reduction of metal precursors in ethylene glycol (EG) which act as a reducing agent at different ratios, followed by addition of hydrogen peroxide (H₂O₂) and subsequently heating the mixture to a refluxing temperature at 473–593 K for several hours. In the alcohol reduction method metal ions are decreased to form metal colloid (zero valent oxidation state) using ethylene solvent after receiving electrons from ethylene glycol, which decomposes to glycolic acid. The advantage of polyol method is that glycolic acid is deprotonated to form glycolate anion which acts as stabilizer for metal colloids in alkaline medium [119- 120]. Sodium hydroxide played a vital role by adjusting the
pH of the reaction solution to control particle size growth for several hours for nanoparticle formation [121].


2.8.1. Electrodeposition

Electrodeposition is also known as the electroplating and these two words are utilized interchangeably. Electrolytic deposition is an electrochemical process that consists in the formation of thin film layer of one metal on top of a different metal coating on the surface of conductive substrate or semi-conducting electrodes immersed in an electrolyte [122–123]. These electrodes are called the working electrode (glassy carbon electrode is used as a cathode), consisting of the catalyst nanoparticles on the surface and the counter-electrode (platinum electrode is used as the anode), it’s where a catalyst isolates negatively charged electrons from positively charged ions to complete the electrical circuit.

2.8.2. Spin coating

Spin coating is a fast and easy method that involve depositing of a metal nanoparticle onto the surface of the electrode. This method is currently used to produce uniform thin layer and homogeneous organic films onto the focal point of a flat substrate, which is then rotated at fast speed typically around 3000 rpm to spread the fluid by centrifugal force [124]. Centripetal acceleration will cause the solution to be spread out and leave a uniform coating of a thin film of resin onto electrode surface [125]. Moreover, the thickness of the film will depend on the concentration of the solvent or nature of the resin such as viscosity, drying rate, percent solids and surface tension.

2.8.3. Drop coating

Drop-coating is a simple, low-cost, versatile method that involves dropping of small droplet of the metal nanoparticles solution with volatile solvent on the electrode surface and then allowing it to dry for a certain period [126]. The solvent will starts evaporating from the top surface of the electrode or heat the substrate to speed up the evaporation process and the catalyst nanoparticles form a non-uniform thin
solid film into dry pore space. Film thickness depends on the concentration of the solvent and the casting solution [127].

2.8.4. Dip-dry
Dip Coating method was developed in the early 80’s to improve high index resistance lenses. In this process the electrode is slowly dipped into the precursor solution for a certain period to leave sufficient interaction time with a uniform velocity of the electrode, to obtain a uniform coating material for complete wetting [128]. Then the electrode is pulled upward on the solution at a constant velocity and the excess liquid will drain leaving out dried thin film on the electrode surface. This thin film can be promoted by sintering step or heat drying to burn out accompanying chemical reactions such as functional oxides.

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Chapter 2: Literature Review


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CHAPTER 3
Experimental procedure

In this chapter, experimental procedure and characterization techniques used in the physical and electrochemical characterization of the electro-catalysts (commercial and/or synthesized) studied were discussed. The crystalline structure, particle sizes, morphologies and functional groups of carbon nanofibers supported palladium nanoparticles and palladium based bimetallic electro-catalysts were characterised using X-Ray Diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy.

Electrochemical characterization of the electrocatalysts and their potential as catalyst for direct alcohol fuel cell oxidation in alkaline media were carried out using different electroanalytical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). The chapter also provides some fundamental quantities measured during the electrochemical experiments such as oxidation potential, peak current and charge transfer at the electrodes.

3.1. Materials and methods

3.1.1. Materials

Table 3.1: Materials and chemicals used in this study

<table>
<thead>
<tr>
<th>Material and Chemicals</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (99.9% CH₃OH)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethanol (99.9% CH₃CH₂OH)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Hydrogen peroxide (30% H₂O₂)</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Ethylene glycol (EG)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Nafion solution 20 wt.%</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Ferrocene</td>
<td>Merck</td>
</tr>
<tr>
<td>Potassium hydroxide pellets (KOH)</td>
<td>Merck</td>
</tr>
<tr>
<td>Palladium (ii) chloride (PdCl₂)</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
3.1.2. **Synthesis of carbon nanofibers**

Carbon nanofibers with worm-like morphology were prepared with a chemical vapour deposition method (CVD) as reported in the literature [1]. Chicken oil was used as the cheap carbon source and ferrocene (C_{10}H_{10}Fe) as a catalyst for the growth of CNFs. The chicken oil was obtained by heating chicken skin in an oven at 300 °C to extract oil from its fat. The liquid oil was mixed with ferrocene in a small beaker under stirring conditions for 15 min and was transferred onto a silicon substrate (dimensions = 20×20 mm, 2mm thickness) which was placed inside a quartz tube (45 mm inner diameter and 500 mm long) and mounted inside an electric furnace. The furnace was then programmed to heat at a temperature of 600 °C under the flow of dilute gas (acetylene and nitrogen) for 1 h. A black deposit was allowed to cool down at room temperature and then mechanically crushed to a fine powder (CNFs). A 100 mg of CNFs was treated in a round bottom flask with 10 mL of a 30% hydrogen peroxide solution under reflux for 4 h to introduce the functional groups. The acid-treated CNF was filtered and subsequently dried in an oven at 120 °C for 2 h. The activated carbon nanofibers were characterised using HR-TEM, FTIR, Raman spectroscopy, X-ray diffraction and X-ray photo- electron spectroscopy.

3.1.3. **Synthesis of Pd/CNFs electro-catalyst**

A 10 mg of PdCl₂ and 90 mg of CNFs were dispersed in 10 mL ethylene glycol solution and then ultrasonicated for 30 min. The subsequent mixture was refluxed for 4 hours under stirring for accomplish depletion of the metal charged particles. The solid electro-catalyst formed as a deposit in the mixture was filtered using

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruthenium(iii) chloride, anhydrous (RuCl₃)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Nickel nanoparticles (Ni)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Commercial standard Pd/C (10 wt.% Pd)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1.0, 0.3- and 0.05-Micron Gamma and Alpha Micropolish Alumina</td>
<td>Buehler, USA</td>
</tr>
</tbody>
</table>
Millipore filter system, washed several times with ultra-pure water to eliminate residual chloride and the solid was placed in a vacuum drying oven at 120 °C for 3 hours to acquire Pd/CNFs electro-catalyst.

3.1.4. **Synthesis of Pd-Ru/CNFs electro-catalyst**

The Pd-Ru/CNFs electro-catalyst was synthesized by alcohol reduction method. In this procedure, 90 mg of carbon nanofibers were dispersed and refluxed in ethylene glycol solution. The metal precursors (6 mg of PdCl₂ and 4 mg of RuCl₃) were simultaneously added to the carbon nanofibers mixture. The subsequent mixture was refluxed for 4 hours under stirring for accomplish depletion of the metal charged particles. The solid electro-catalyst formed as a deposit in the mixture was filtered using Millipore filter system, washed several times with ultra-pure water to eliminate residual chloride and the solid was placed in a vacuum drying oven at 120 °C for 3 hours to acquire Pd-Ru/CNFs electro-catalyst.

3.2. **Characterization of the prepared electro-catalyst**

3.2.1. **Transmission Electron Microscopy (TEM)**

HRTEM is a powerful technique that is used to determine particle size, compositional and morphology of the composite material [2]. TEM studies were performed on a JEOL JEM 2100 instrument with an acceleration voltage operated at 200Kv, fitted with a Gatan CCD camera. The electro-catalysts powders were dispersed in ethanol solution which was then ultrasonicated for 15-20 minutes. The small amount of the prepared electro-catalyst powder solution was dropped onto the copper grid coated with a lacy carbon film. The prepared sample was air-dried to evaporate ethanol at room temperature. Samples were then mounted in a sample holder, which was introduced directly to the shaft of the TEM for measurements.
3.2.2. Scanning electron microscopy

Scanning electron microscopes was utilized to acquire surface images and determine the elemental composition of the metal nanoparticle agglomerates. SEM studies were performed on a JEOL SEM 2100 Field Emission Scanning Electron Microscope instrument outfitted with a LaB6 source used in imaging and EDS mode. SEM operates with an electron gun as a light source with condenser lenses and objective lenses present in the system. A fine beam of electrons is scanned across the surface of the specimen with a detector monitoring the intensity of the secondary signal from the sample.

3.2.3. X-ray photoelectron spectroscopy (XPS)

XPS is a surface analytical technique that is utilized to measures both elemental and chemical oxidation state of the elements that exist within a material [3]. XPS was carried out on a Kratos Axis Ultra DLD, using an Al (monochromatic) anode,
equipped with charge neutralizer. The operating gas pressure in the chamber was kept from $10^{-2}$ to 1 Torr. For wide/survey XPS scans, the accompanying parameters were utilized; emission current was kept at 12.5 mA and the anode (HT) voltage at 15 kV. The resolution utilized to obtain wide/survey scans was at 160 eV pass energy utilizing a hybrid lens in the slot mode. For the high-resolution scans, the resolution was changed to 40 eV pass energy in the slot mode. A small amount of electro-catalyst powder was suspended in alcohol deposited on a piece of Silicon substrate and dried on air for the XPS analysis. The peak asymmetry of the metallic surface state was described by utilising a sample of pure palladium after reduction under hydrogen gas. The binding energy was calibrated using carbon peak shifting of Multipak (R) software at 284.6 eV as a reference before curve fitting.

3.2.4. X-ray powder diffraction (XRD)

XRD is a powerful non-destructive technique that is used to study the crystal structure, particle size and the amorphous nature of the electro-catalysts by their x-ray diffraction or scattering patterns [4]. Approximately 2 g of Pd nanoparticle powder was loaded onto a stainless-steel sample holder and inserted into the XRD chamber. XRD patterns of deposited Pd nanoparticles were obtained on a PANalytical X’Pert Pro powder diffractometer using a Cu Kα radiation ($\lambda=0.15405$ nm) at 40 kV and 40 mA operational conditions. The measurements were conducted at a scan speed of 0.075 2θ/min and a scan step of 0.02 in the 2θ range from 5 to 90° to cover the strong diffraction peaks (111), (200) and (220) of crystalline Pd particles. The Pd (111) crystalline plane was used to calculate the crystallite size average of Pd nanoparticles according to the Debye-Scherrer equation [5] and the full width at half maximum (FWHM) of the peak.

$$D = \frac{k \times \lambda}{FWHM \times \cos \theta}$$

In this equation, $D$ is the particle size (nm), $k = 0.89$ for spherical particles is the shape factor, FWHM is the full width of the peak at half maximum, $\lambda$ is the wavelength of the X-ray and $\theta$ is the angle of reflection at the maximum of diffraction. Both FWHM and $\theta$ are expressed in radians.
When a beam of X-rays of wavelength $\lambda$ enters a crystal, the maximum intensity of the reflected ray occurs and are calculated using Bragg's equation [6-8]:

$$2d \times \sin \Theta = n \times \lambda$$

Where $d$ is the distance between atomic layers in crystals, $\lambda$ is the wavelength of the incident X-ray beam, and $n$ is an integer ($n = 1$).

![Figure 3.2: Picture of a Philips X'Pert Powder X-ray diffractometer.](image)

3.2.5. **Raman spectroscopy**

Raman spectroscopy is a spectroscopic technique for the analysis of different carbon support material that can be used as electro-catalyst in fuel cells. This technique was utilized to gauge the wavelength and intensity of inelastically scattered light from molecules [9-10]. In Raman spectrometer, the sample was simply presented to a microscope which is an integral part of the spectrometer. It also comes with a probe to hold the sample to be examined. This spectrometer utilizes a high-power density 785 nm laser to excite the molecular vibrations at the sample.
3.2.6. Fourier transform infra-red spectroscopy (FTIR)

FTIR is an analytical technique that is used to study the functional groups present in a compound. It identifies the frequency of band vibration between the bonds of the atoms in a sample with absorption peaks, by measuring the intensity of infrared radiation as a function of wavelength or wavenumber [11-12]. In this experiment, the application of a Perkin Elmer Spectrum 100 spectrometer was used to measure infrared spectra of the functional groups of the carbon nanofibers (CNFs). CNFs sample was placed in the path of an infrared beam, some of the infrared radiation was absorbed by the sample and some of it transmitted and then the light signal penetrated the sample to the detector. The penetration depth of a light beam utilizing an FTIR technique into a sample was around 0.5–3 λm. This measurement only needed little samples of CNFs and the sample was conducted twice to ensure the infrared spectra of the investigated CNFs samples. The observed spectra were the absorbance of the CNFs sample versus the wavenumber range of 4000 cm⁻¹ - 400 cm⁻¹ with a resolution of 4 cm⁻¹.

3.3. Electrochemical studies

For cyclic voltammetry experiment, a Dropsens μSTAT8000 potentiostat single electrochemical cell system (Figure 3.3), using Dropview 8400 software was used to determine the electro-catalytic activities of the synthesized carbon nanofibers supported palladium bimetallic catalysts for methanol and ethanol oxidation in alkaline medium. All electrochemical experiments were done with a three-electrode setup which consists of the necessary electric circuits, a reference electrode (Ag/AgCl), counter electrode (Pt rod) and the working electrode (modified glassy carbon with the catalyst deposited). All electrochemical experiments were made under inert atmosphere by bubbling argon in the electrolyte prior to characterization to prevent reactions between the electrode and dissolved oxygen.
3.3.1. Preparation of the working electrode

A 10 mg of electro-catalyst was dispersed in 1 mL ethanol containing 2 drops of Nafion solution inside the polyethylene container. The resulting solution was sonicated for 15 min to obtain an ink and transferred onto a dried pre-treated glassy carbon electrode. Prior to fabrication, the GC electrode was polished on Micro cloth TM (Buehler) using 1.0, 0.3 and 0.05-micron alumina slurries in sequence and after that sonicated with double distilled water to eliminate free particles from Micro cloth TM (Buehler). Electrochemical investigations were done using a Dropsens potentiostat with a regular three-electrode partition glass cell. The potentials of the working electrode were measured utilizing the reference (Ag/AgCl /3 M NaCl) and counter electrodes (Pt wire). All outcomes were contrasted with commercial 10 %wt Pd/C electro-catalyst tested at the same conditions. Ten CV cycles or scans were performed for all modified electrodes and only the 10th scan was reported.
3.3.2. Voltammetry

3.3.2.1. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) was performed to determine the electro-catalytic activity of the nanocatalysts and electrode surface reactions [14]. It helps electrochemist to understand the behaviour of active electrochemically species and the performance of the electro-catalyst. The behaviour of the electro-catalysts in alkaline media was measured in a three-electrode half-cell. The working electrode was a modified glassy carbon with the catalyst ink deposited. The potential was applied with an Dropsens μSTAT8000 potentiostat single electrochemical cell system using Dropview 8400 software. All experiments were carried out at room temperature (25°C). Ethanol and methanol were also used as an electrolyte to determine the activity of the electro-catalysts towards the ethanol and methanol electro-oxidation reactions. Prior to measurements, the electrolyte was purged with argon gas for 30 minutes to remove dissolved oxygen. The surface of the electrode was then conditioned at a scan rate of 50 mV/s vs. Ag/AgCl with scan potential from -0.8 to 0.4 V for 50 cycles. The voltammograms of the palladium electro-catalysts prepared in this work will be discussed in Chapter 4 and 5.

3.3.2.2. Chronoamperometry (CA)

Chronoamperometry (CA) is an electrochemical technique that is like CV and it is used to study the stability as well as the poisoning rates of the fuel cell electrodes. However, the applied potential of the working electrode is stepped directly to -0.2 V, but not scanned unlike the CV and the current resulting from faradaic processes versus time measurements which determines the time dependence of the current at which the concentration of electroactive species becomes steady is measured [15].

Chronoamperometric (CA) experiments were conducted in a solution of 1 M KOH + 1 M ethanol over a time of 2000 s at a scanning rate of 10 mV/s to study the behaviour and stability of the electro-catalysts during continuous operation.
3.3.2.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful experimental technique that is used to study the electrochemical system response of alcohol electro-oxidation processes in fuel cells [16-17]. The impedance study of the three palladium electro-catalyst was conducted in the frequency range 0.01 - 10 x 10^3 Hz at a consistent dc potential, 0.2 V vs RHE in 1 M KOH + 1 M (CH_3CH_2OH and CH_3OH). This technique works by first polarizing the electrochemical cell at a fixed voltage and then applying an AC potential to perturb the system. The response to this potential is an AC current signal. The AC voltage and current response of the fuel cell was analyzed by the frequency response analyzer to determine the resistive, capacitive and inductive behaviour impedance of the cell. EIS experiments are interpreted using an “equivalent circuit” of resistors and capacitors [18]. Equivalent circuit modeling of EIS data was used to extract physically meaningful properties of the electrochemical system by modeling the impedance data in terms of an electrical circuit composed of ideal resistors (R), capacitors (C), and inductors (L).
References


4.1. Introduction

Carbon nanomaterials are of growing interest in the fuel cell environment due to their promising applications [1]. The support for metal nanoparticles includes carbon nanotubes (CNTs), carbon nanodots (CNDs), graphene (G) and carbon nanofibers (CNFs). The low cost and availability make the carbon nanofiber composite materials the most used support for electro-catalysts in low-temperature fuel cells [2]. CNFs have inspired powerful research over the past years due to their good electrical, thermal conductivity and high stability in the field of physics, chemistry, nanotechnology and material sciences [3]. Carbon nanofibers and nanotubes have similar circular shape, however, CNFS have a larger diameter of approximately 100–500 nm and different morphology [4]. Carbon nanofibers appear to be the most promising support material in direct alcohol fuel cell due to a large surface area which allows for high metal dispersion. The most important two methods developed to synthesize CNFs include electrospinning polymeric nanofibers and chemical vapor deposition (CVD). Electrospinning is a technique that uses high voltage as the carbonization process for polymer solutions [5–7], while CVD is a chemical process that uses iron, cobalt, nickel as catalyst and hydrocarbon gases such as acetylene and nitrogen for growing CNFs [8–10].

Direct alcohol fuel cells (DAFCs) are gadgets in which the chemical energy stockpile in small alcohol molecules is directly converted into electrical energy via electrochemical reactions [11]. The interest is greater in direct alcohol fuel cells because the utilization of liquid fuels streamlines the fuel conveyance framework, contrasted with hydrogen-fed fuel cells [12–14]. The DAFC is the most advanced
technology for stationary applications, power sources for transportation and portable electronics [15,16]. However, so far methanol cannot be considered as a candidate for stationary and mobile low-temperature energy production in fuel cells because of its volatility, toxicity and methanol hybrid from the anode to the cathode side, therefore it is not thought as a favorable and friendly fuel [17,18]. Furthermore, methanol oxidation leads to the degradation of the electrode due to the formation of carbon monoxide. Ethanol has numerous preferences over hydrogen, methanol and formic acid because of its financial and ecological qualities, with higher energy density, higher boiling point for safer storage in transportation applications and lower toxicity than those of methanol [19,20]. More importantly, ethanol as a green fuel can be easily created in large amounts from biomass by fermentation of sugar-containing crude materials [21]. However, the accomplish ethanol electro-oxidation to carbon dioxide is more troublesome as compared to the case of methanol because of the prerequisite of C-C bond breaking and the generation of CO-like species that toxin platinum electro-catalysts [22,23]. Moreover, alkaline oxidation of ethanol is an alternative to methanol since it allows the use of other, less noble metals such as palladium, ruthenium, nickel, and tin than the expensive platinum electro-catalyst [24].

The less expensive palladium catalysts have been studied and shown to show higher activities and poisoning resistances for electro-oxidation of ethanol than platinum in alkaline media. Furthermore, the mixing of palladium with different metals as co-catalysts enhances its action, stability and toxic substance resilience [25].

4.2. Results and discussion

4.2.1. Characterization of nanoparticles

4.2.1.1. Transmission electron microscopy

Structural details of carbon nanofibers were examined by TEM. The pictures of the nanofibers synthesized from the chicken skin fat revealed a worm-like morphology with a diameter of an approximately 300-500 nm (Figure 4.19(a)). The
synthesized CNFs are slightly different in morphology to the one's reported by Suriani et al [4]. This difference can be attributed to the mixing ratio between chicken oil and the catalyst and different carbonization temperatures [26,27]. The TEM image of Pd/CNFs electro-catalyst shown in Figure 4.19(b), displayed a successful attachment of palladium nanoparticles (Pd NPs) onto the surface of the functionalized carbon nanofibers, proposing an electrostatic interaction between Pd nanoparticles and the carboxylic group of CNFs. In Figure 4.19(c), the Pd NPs gave an average size of 9.3 nm which was evaluated using ImageJ software. However, some of the Pd nanoparticles were agglomerated in the Pd/CNFs electro-catalyst.
4.2.1.2. Fourier transform infrared spectroscopy

The FTIR spectrum of the carbon nanofibers showed the presence of hydroxyl and carboxylic acid groups on the sample surface (Figure 4.2). CNFs had characteristic absorption bands at 3433 cm\(^{-1}\) and 2915 cm\(^{-1}\) ascribed to the O-H of carboxyl groups [28]. The characteristic vibrations at 2855 cm\(^{-1}\) and 1389 cm\(^{-1}\) are assigned to the aliphatic -CH and -CH\(_2\) groups of the CNFs [29]. The band that appeared at 1725 cm\(^{-1}\) is ascribed to the C=O stretching vibrations of carbonyl groups of the carboxylic acids [30]. Lastly, the band at 1584 cm\(^{-1}\) corresponds to a C=C stretching originated from the preparation of CNFs by the process of carbonization and graphitization at high temperatures [31].

Figure 4.1: TEM images of (a) CNFs (b) Pd/CNFs and (c) average particle size of Pd NPs.

Figure 4.2: FT-IR spectrum of CNFs.
4.2.1.3. **Raman spectroscopy**

The Raman spectrum of the carbon nanofibers *(Figure 4.3)* consists of two peaks D and G bands at 1335 and 1572 cm\(^{-1}\), which correspond to the disordered carbon peak (D) and graphite peak (G) \([32,33]\). The D band is attributed to the K-point phonons of A\(_{1g}\) symmetry which resulted from the vibration mode of the structural defect, while the G band represents first-arrange scattering of the E\(_{2g}\) vibration mode attributed to the vibration of sp\(^2\)-bonded carbon \([33,34]\). These bands are assigned to the C–C bond stretching mode in the defective or disordered graphite layers \([4]\). The acquired spectrum can be attributed to amorphous disordered graphitic carbon because the D-band was wide and the full width of the G-band at half maximum was 55.8 cm\(^{-1}\). The intensity ratio of the CNFs calculated in the spectrum D to G band (ID/IG) was 0.91 which constitute the degree of crystallinity with large defects of carbonaceous material.

![Raman spectrum of CNFs](image_url)

*Figure 4.3:* Raman spectrum of CNFs.
4.2.1.4. X-ray diffraction spectroscopy

The crystalline structure of CNFs and Pd/CNFs was characterized using X-ray diffraction technique and the typical diffraction peaks are presented in Figure 4.4. The XRD results revealed that the structures of CNFs and Pd/CNFs were polycrystalline carbon consisted of defective graphitic crystal lattice [32]. Intense and sharp diffraction peak at 25.5° indexed with (002) for the CNFs is due to graphitic carbon material [35]. The other six peaks that are present in the sample based on the XRD pattern at 2θ = 30.0°, 35.5°, 43.0° and 53.5°, 57.0°, 62.5° were identified to be iron carbide (Fe₃C) and iron oxide (Fe₃O₄) respectively [4]. The iron particles were attributed to the ferrocene catalyst used during the synthesis or growth of carbon nanofibers using the chemical vapor deposition method. The Pd/CNFs composite material showed 2θ strong diffraction signals at 40.0°, 46.8° and 68.5° ascribed to Pd (111), Pd (200) and Pd (220) respectively [36]. It should be noted that the emergence and prominence of a new peak at 2θ = 40.0° in the Pd/CNFs nanocomposite confirmed successful introduction of Pd nanoparticles. The Pd (111) crystalline plane was utilized to compute the average crystallite size of palladium nanoparticles according to the Debye-Scherrer equation [37,38]:

\[ D = \frac{k \times \lambda}{\text{FWHM} \times \cos \theta} \]

In this equation, D is the particle size (nm), k = 0.89 for spherical particles, FWHM is the full width of the peak at half maximum, \( \lambda = 0.154 \) is the wavelength of the X-ray and \( \theta = (111) \) is the angle of reflection at the maximum diffraction. The obtained palladium nanoparticle size was 62.6 nm.
Figure 4.4: XRD patterns of CNFs and Pd/CNFs electro-catalyst.

4.2.1.5. X-ray photoelectron spectroscopy

The surface chemistry and the electronic structures of the Pd/CNFs electro-catalyst were investigated by XPS. As demonstrated in Figure 4.5 (a), XPS survey spectra of the Pd/CNFs confirmed the existence of carbon (C 1s at 284.0 eV), oxygen (O 1s at 531.0 eV) and palladium (Pd 3d at 335.0 eV) on the surface [39]. Figure 4.5 (b) illustrates the high-resolution C 1s spectrum for CNFs which can be deconvoluted into five individual segment peaks at 284.3, 285.5, 286.8, 288.4 and 290.6 eV. The C1s peak at 284.3 eV and 285.5 eV correspond to the sp$^3$ and sp$^2$ hybridized carbon C-C and C=C in the graphite structure respectively while the weak broad peaks at 286.8, 288.4 and 290.6 eV are assigned to the binding energy of C–O, C=O and COOH bonds [40,41]. As presented in Figure 4.5 (c), the high-resolution O 1s spectrum for CNFs shows the coexistence of two peaks at 529.9 and 531.3 eV which are ascribed to the C–O and C=O respectively. The peaks at 532.9, 534.2 and 535.9 eV are attributed to the C-O-H/C-O-C and (COOH) carboxylic group. The synthesized CNFs are functionalized with the
carboxylic acid group in view of the XPS outcomes, which concurred with the literature [30,42]. These XPS data are in good agreement with the FTIR analysis. Figure 4.5 (d, e and f) present the XPS spectra of the Pd/CNFs electro-catalyst. The C 1s and O 1s XPS spectra in Figure 4.5 (d and e) for Pd/CNFs electro-catalyst displayed the presence of six peaks. The high-resolution Pd 3d spectrum in Figure 4.5 (f) showed two signals each with three pairs of asymmetric peaks: the first pair at 335.2, 336.6 and 340.5 corresponding to Pd 3d5/2 signal of bulk Pd (0) species in a metallic state [36]. The other pair of asymmetric peaks at 336.2, 341.9 and 343.4 eV attributed to Pd 3d3/2 signal from Pd-oxide species. The binding energies of the palladium metal from the XPS outcomes are in great concurrence with reported values in the literature [43,44].

![Figure 4.5: XPS spectra of: (a) CNFs and Pd/CNFs survey (b) C 1s of CNFs, (c) C 1s of Pd/CNFs, (d) O 1s of CNFs, (e) O 1s of Pd/CNFs, (f) Pd 3d spectra for Pd/CNFs electro-catalyst.](image-url)
Table 4.1. Elemental composition of CNFs and PD/CNFs acquired from XPS data.

<table>
<thead>
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<th>Sample</th>
<th>C%</th>
<th>O%</th>
<th>Pd%</th>
</tr>
</thead>
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<tr>
<td>CNFs</td>
<td>90.55</td>
<td>9.45</td>
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</tr>
<tr>
<td>Pd/CNFs</td>
<td>85.97</td>
<td>11.68</td>
<td>2.35</td>
</tr>
</tbody>
</table>

4.2.2. Application of electro-catalyst for electro-oxidation of ethanol

4.2.2.1. Cyclic voltammetry

The result of the electrocatalytic oxidation of ethanol using the synthesized catalysts is presented in Figure 4.6. Carbon nanofibers had no catalytic activity towards 1.0 M ethanol electro-oxidation in alkaline medium (1.0 M potassium hydroxide). The Pd/CNFs and Pd/C modified GC electrodes showed two distinctive oxidation ethanol peaks on the forward and reverse scans. The forward sweep is related to the electro-oxidation peak of freshly chemisorbed ethanol molecules and the reverse sweep is related with the expulsion of the residual carbon species formed in the positive sweep [45]. The larger the electro-oxidation peak current in the positive sweep the less intermediate products formed, and this indicates the effectiveness of the electro-catalyst performance for the oxidation reaction of the ethanol [46]. The current density for Pd/CNFs electro-catalyst is 1160 μA cm⁻² which is greater than 440 μA cm⁻² of the commercial Pd/C electro-catalyst in alkaline conditions. The onset potential of the electro-catalyst for the electro-oxidation of ethanol was −6.0 V for Pd/CNFs and −5.0 V for Pd/C respectively. Thus, Pd/CNFs has a lower onset potential than Pd/C, demonstrating that in ethanol oxidation, Pd/CNFs is a more dynamic electro-catalyst than Pd/C and this is in concurrence with a related report revealed in the literature [47]. This might be credited to the large surface area due to high palladium dispersion provided by the carbon nanofibers support material [48]. The proportion of the forward peak current (Iᶠ) to the backward peak current (Iᵇ), is generally utilized to measure the poisoning tolerance resulted by intermediates products during electro-oxidation [49–51]. The Iᶠ/Iᵇ ratio for Pd/CNFs electro-catalyst is 2.15 displaying greater catalytic poisoning tolerance of this electro-catalyst in ethanol.
compared to 1.15 of commercial Pd/C electro-catalyst. Compared to the literature review, the so-acquired Pd/CNFs showed better catalytic activity (1160 μA cm⁻²) for ethanol electro-oxidation in alkaline conditions with 2.35% palladium loading which was determined by the XPS technique. The CNFs obtained from waste chicken fat are cheaper support materials for electro-catalysts as compared to those prepared from polyacrylonitrile (PAN nanofiber), cobaltocene + ferrocene (CoFe₂O₄ nanoparticles) and calcium carbide (CaC₂) + water [29,52,53]. It has been reported that higher current densities for Pd/CNFs electro-catalyst towards electro-oxidation of alcohol in alkaline solutions were also observed by Guo et al. [54] and Nitze et al. [55], but less than our synthesized Pd/CNFs electro-catalyst.

Figure 4.6: Cyclic voltammetry graphs for CNFs, Pd/C, and Pd/CNFs catalysts in 1.0 M CH₃CH₂OH solution in alkaline medium (1.0 M KOH) at a scan rate of 50 mVs⁻¹ at room temperature.
4.2.2.2. Chronoamperometry

Chronoamperometry is the best electro-analytical method used in electrochemistry to study the stability and poisoning rates of the electro-catalyst [56]. Figure 4.7 presents the chronoamperometric curves for the synthesized Pd/CNFs and Pd/C electro-catalysts towards electro-oxidation of ethanol in alkaline solutions. The steady state current densities of Pd/CNFs and Pd/C electro-catalysts were 39.1 μA cm\(^{-2}\) and 8.87 μA cm\(^{-2}\) after 2000 seconds at the potential of 0.5 V. It was evident that the current density for Pd/CNFs was substantially bigger when contrasted with the commercial Pd/C in electrochemical oxidation of ethanol, showing the enhanced electro-catalytic stability of Pd/CNF modified electrode. Also, from Figure 4.7 a sharp current decay was observed for Pd/C electro-catalyst in the alkaline medium than Pd/CNFs, which could be due to ethanol intermediates which are poisoning the palladium electro-catalyst [57]. Therefore, the Pd/CNFs electro-catalyst was more effective and poisoning tolerant contrasted with the commercial palladium nanoparticles in activated carbon (Pd/C).
4.2.3. Application of electro-catalyst for electro-oxidation of methanol

4.2.3.1. Cyclic voltammetry

Figure 4.8 presented CV curves of CNFs, Pd/CNFs and Pd/C GC electrodes in 1.0 M KOH + 1.0 M CH$_3$CH$_2$OH solution. As illustrated in Figure 4.8, carbon nanofibers had no electro-catalytic activity towards methanol oxidation in alkaline conditions. The results showed that CNFs with Pd nanoparticles have high electro-catalytic performance towards electro-oxidation of methanol in alkaline conditions compared with commercial palladium nanoparticles supported on activated carbon (Pd/C). The enhanced performance for Pd/CNFs electro-catalyst can be attributed to the large surface area and the successful dispersion of Pd.
nanoparticles on the carbon support material [58]. The peak potential of Pd/CNFs electro-catalyst at -1.25 V in the forward sweep was ascribed to the chemisorbed species from methanol oxidation [58,59]. Another peak potential of Pd/CNFs electro-catalyst at -3.5 V with current intensity 290 µA in the reverse sweep was related with the oxidation of carbonaceous species of unreacted methanol [60–62]. The peak current density is 1212 µA cm\(^{-2}\) for Pd/CNFs electro-catalyst and was much larger or twice that of Pd/C electro-catalyst (624 µA cm\(^{-2}\)), indicating a remarkably enhanced catalytic activity of Pd/CNFs electro-catalyst.

![Cyclic voltammetry graphs](image)

**Figure 4.8:** Cyclic voltammetry graphs of CNFs, Pd/CNFs, and Pd/C catalysts in 1.0 M KOH + 1.0 M CH\(_3\)OH solution at a scan rate of 50 mVs\(^{-1}\) at room temperature.

When compared results in **Figure 4.6** and **4.8**, the catalytic activity of Pd/CNFs and Pd/C towards electro-oxidation of ethanol in alkaline conditions was observed to be lower than that of Pd/CNFs and Pd/C in methanol oxidation reactions. Also, comparing the current density and onset potential of these alcohol molecules, the
activity of Pd/CNFs and Pd/C towards the electro-oxidation of methanol is better than the activity in ethanol electro-oxidation reactions. This could be because of the need of dissociative chemisorptions of ethanol molecule throughout electro-oxidation reaction in which adsorption of strongly adsorbed intermediates, among which COads is one of the poisoning species that contaminate the electrode [63].

4.2.3.2. Chronoamperometry

Chronoamperometry was utilized to assess the prolonged stability of palladium electro-catalysts towards 1.0 methanol oxidation in alkaline medium [64,65]. Figure 4.9 presents the chronoamperometry curves for Pd/CNFs and Pd/C GC modified electrode after a decay of 2000 s at the potential of 0.5 V. The synthesized Pd/CNFs electro-catalyst was observed to have a current density (48.19 μA cm\(^{-2}\)) that was approximately 3 times higher when contrasted with the Pd/C electro-catalyst (12.88 μA cm\(^{-2}\)). It can be concluded that Pd/CNFs electro-catalyst showed higher stability with low poising rate compared to Pd/C electro-catalyst for both ethanol and methanol oxidation reactions. The chronoamperometry results strongly agreed with the results obtained from cyclic voltammetry.
Figure 4.9: Chronoamperometry of Pd/C and Pd/CNFs electro-catalysts in 1 M KOH + 1 M CH₃OH.
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Chapter 4: Results and discussions.


CHAPTER 5

Palladium-Ruthenium alloy nanoparticles supported on carbon nanofibers as anode catalysts for methanol and ethanol electro-oxidation in alkaline media.

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5.1. Introduction
Development of an anode electro-catalyst for direct alcohol fuel cells (DAFCs) that employ liquid hydrocarbon fuels, for example, ethanol and methanol in alkaline medium are greatly acknowledgeable throughout the economy and fuel cell environment [1,2]. DAFC is a device in which the chemical energy stored in little alcohol molecules is straightforwardly converted into electrical energy via electrochemical reactions. Due to low cost, simple handling, storage and high energy density, ethanol and methanol are the most popular used fuels among other alcohols in DAFCs [3,4]. The performance of a DAFC depends on the catalyst activity and lifetime [5]. An electro-catalyst is a type of catalyst that can speed up the rate of an electro-chemical reaction occurring on an electrode surface without being consumed in the process [6,7]. The high expense of the platinum electro-catalyst in the fuel cell environment should be mitigated by using other platinum group metals (PGMs) for example, Palladium (Pd), Ruthenium (Ru), Nickel (Ni) and Molybdenum (Mo) [8,9]. Palladium metal is less expensive and 50 times more abundant compared to platinum metal on earth. In electro-catalysis, Pd metal is the most active catalyst among these PGMs towards alcohol electrooxidation in alkaline conditions showing better tolerance to the CO intermediate [10]. Alloying palladium catalyst with second or third metal catalyst produces lower oxidation potential and replacement sites for the electrooxidation reactions [11,12]. The problem of the slow alcohol oxidation rate has been reduced to some extent by alloying Pd with a non-precious metal such as Ru, Sn, Ni, Cr or Mo etc [13]. It is believed that the electro-catalytic activity of the catalyst can be enhanced by alloying these transition metals when developing a binary or a ternary electro-catalyst [14,15]. Many studies have shown that the addition of ruthenium to platinum in acidic media could improve the catalytic activity by
escalating resistance towards the contamination of the Pt catalyst surface by strongly intermediate carbonaceous material [16]. Among the bimetallic electro-catalysts studied, the Pd-Ru is regarded as the most efficient catalyst towards methanol and ethanol oxidation in a basic environment with enhanced CO tolerance [17]. This enhancement in catalytic activity of Pd-Ru/C is described by a bifunctional mechanism as observed on Pt-Ru catalysts: (i) Ru promotes electro-oxidation of ethanol to carbon dioxide due to surface oxygen-containing species to adsorbed strongly carbonaceous intermediate on the platinum catalyst and (ii) Ru also modifies platinum electronic structure by mitigating CO poisoning while binding hydroxyl groups to the ruthenium sites at a lower potential [18,19]. Many studies have shown that Pd-Ru electro-catalysts produces high current densities and low onset potentials using different carbon support materials in alkaline conditions [20,21]. Bagchi and Bhattacharya examined the ethanol oxidation reaction (EO\textregistered) on Pd-Ru composite material in 1 M KOH and showed that the electrodes containing the higher amount of deposit are less influenced by carbonaceous toxic substance [22,23]. Yougui et al. revealed the synthesis of Vulcan XC72 supported Pd-Ru catalysts by an impregnation technique with an atomic Pd: Ru ratio ranging between 1:0 and 1:2. The Pd-Ru/C electro-catalyst demonstrated a higher catalytic activity compared to Pt-Ru/C by a factor of 4 in the range of 0.3 and 0.4 V and a significantly lower onset potential compared to commercial Pd/C [24,25]. Bambagionia et al. have synthesized Pd-Ru composite material supported on multiwalled carbon nanotubes (MWCNTs) by the impregnation-reduction method. The Pd-Ru/MWCNTs electro-catalyst have alcohol oxidation reaction (AOR) activity for glycerol, methanol and ethanol in (2 M KOH) alkaline conditions [26]. However, this anode catalyst is chemically steady just for the electro-oxidation of ethanol. Methanol and glycerol oxidations lead to the formation of carbon monoxide which can possibly poison the electrode [27]. Ethanol is specifically oxidized to acidic acid which before long gets changed into acetate ion [26]. An examination directed by Modibedi et al. reported the catalytic activity of the binary PdSn catalyst and a ternary PdRuSn catalyst deposited on carbon black [28]. These anode electro-catalysts are obtained by using a chemical reduction reaction utilizing sodium borohydride as a reducing agent and investigated towards ethanol oxidation in alkaline conditions. Both binary and
ternary catalysts show an enhanced electro-catalytic activity in ethanol reactions than commercial PtRu/C and Pd/C, however, a ternary catalyst shows a low stability and current density compared to Pd-Sn/C catalyst. The carbon support material also plays a major role in fuel cell architecture; it improves the catalytic activity of the anode and cathode electro-catalysts [29,30]. Carbon nanofibers which were used in this study have attracted much attention because of their high specific surface area, chemical inertness, high electrical and thermal conductivity [31]. In this work, Pd-Ru electro-catalyst supported on carbon nanofibers was prepared utilizing alcohol reduction or polyol method without changing the pH of the solution. The prepared Pd-Ru/CNFs catalyst exhibits higher electro-catalytic activity than Pd/CNFs and Pd/C for both methanol and ethanol oxidation reactions in alkaline media.

5.2. Results and Discussion

5.2.1. Characterization of nanoparticles

5.2.1.1. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)
The morphology and elemental analysis of the Pd-Ru/CNFs were examined using SEM and TEM. Figure 5.1 shows SEM and TEM images of the carbon nanofibers with the length diameter typically ranges from 300 nm to 500 nm and highly dispersed with a large number of palladium-ruthenium nanoparticles. The synthesized CNFs are slightly different in morphology to the ones reported by Suriani et al [32]. This difference can be ascribed to the mixing ratio between chicken oil and the catalyst and different carbonization temperatures [33]. As presented in Figure 5.1 (b)-(c), some of the Pd and Ru NPs are non-uniformly distributed or agglomerated on the Pd-Ru/CNFs composite material. ImageJ software was utilized to estimate the average particle size from 100 particles in random regions. Based on the measurement of 100 particles selected from random regions, the distribution of Pd-Ru nanoparticle sizes shown in Figure 1d above is calculated to be 9.8 nm. As can be seen in Figure 5.2(a), the SEM elemental mapping analysis shows the presence of the Pd, Ru, C and O elements on the Pd-Ru-CNFS electro-catalyst. Carbon and the small amount of oxygen were obtained from the carbon nanofiber support material. The dispersion of Pd and Ru match well, indicating the successful synthesis of a composite and the full attachment between Pd and Ru phases. Carbon is dispersed over the whole of CNF support material, and relatively small amounts of oxygen are detected. Energy dispersive x-ray (EDX) results reveal the presence of Pd, Ru and C, confirming the successful preparation of palladium-ruthenium nanoparticles supported on carbon nanofibers surface as demonstrated in Figure 5.2(b).
5.2.1.2. **X-ray diffraction spectroscopy (XRD)**

XRD was conducted to investigate the crystalline structure and interaction between Pd and Ru in the Pd-Ru/CNFs electro-catalyst. The XRD patterns of the prepared CNFs supported Pd and Ru NPs sample are shown in Figure 5.3, below. The intense and sharp diffraction peak for the three samples at $2\theta = 25.5^\circ$ indexed with C (002) reflection is due to graphitic carbon material. The other three diffraction peaks of the graphitic carbon material at $2\theta = 42.6^\circ$, $51.8^\circ$, $76.8^\circ$ are associated with carbon facets C (100), C (004), and C (110), respectively [34]. The XRD pattern for Pd/CNFs shows $2\theta$ strong diffraction signals at $40^\circ$, $46.8^\circ$, $68.5^\circ$ and $82^\circ$. These diffraction signals are ascribed to palladium facets with orientations Pd (111), Pd (200), Pd (220) and Pd (311) [35]. The Pd (111) crystalline plane has been studied as the most highly active facets for electro-oxidation of ethanol and methanol in alkaline conditions with low poisoning rate [36]. The XRD patterns of Pd-Ru/CNFs in Figure 5.3, shows four diffraction peaks at $40^\circ$, $46.8^\circ$, $68.5^\circ$ and $82^\circ$ which are corresponding to the (111), (200), (220) and (222) facets of fcc Pd-Ru nanoparticles [37]. The diffraction planes attributed to the Pd-Ru nanoparticles supported on CNFs slightly shifted to higher $2\theta$ values than Pd NPs supported on CNFs due to the alloying of ruthenium metal particles [38].

**Figure 5.2**: (a) SEM-EDS mapping images of Pd-Ru/CNFs (b) EDX scan of the Pd-Ru/CNFs.
The diffraction peaks observed for the Pd-Ru/CNFs electro-catalyst are wider than that of Pd/CNFs showing a reduction in particle size and increment in the lattice parameter of palladium [38]. Furthermore, there are no diffraction planes related to Ru, showing that Ru is alloyed to palladium structure. A high level of alloying between Pd and Ru NPs has revealed to offer a better electro-catalytic activity in Pd-Ru/CNFs.

**Figure 5.3:** XRD patterns of CNFs, Pd/CNFs and Pd-Ru/CNFs electro-catalyst.

5.2.1.3. **X-ray photoelectron spectroscopy (XPS)**

XPS analysis was utilized to examine the oxidation states of Pd and Ru in the surface layers of Pd-Ru/CNFs composite material. **Figure 5.4(a)** shows the XPS survey spectrum and the deconvoluted spectra for the significant element of the prepared electro-catalyst. The survey spectrum demonstrates the major signals for C 1s, O 1s, Ru (3s, 3p, 3d, 4d), Pd 3d, and the traces of N 1s and Si 2p. The deconvoluted peaks of the C 1s + Ru 3d for Pd-Ru/CNFs electro-catalyst show the
existence of 5 peaks in **Figure 5.4(b)**, C 1s was fitted with 4 Voigt-type singlets and a Shirley-type background was also added to the overall fit. The binding energy peaks with respect to the overall % area of the core level at 284.46 eV, 34% and 285.62 eV, 36% are attributed to the C-C and C=C bonds respectively while the binding energy peaks at 286.78 eV, 24% and 289.85 eV, 6% eV are ascribed to the carboxylic groups [35,39]. The peak at 281.98 eV is assigned to the binding energy of Ru 3d5/2. The Ru 3d spectrum was chosen for Ru because of its high intensity despite the fact that it overlaps with the C 1s peaks. Ru 3d is composed of a single spin-orbit doublet (3d5/2 and 3d3/2, isolated by a spin-orbit splitting of 4.2 eV) - i.e [40,41]. Ru is present in one oxidation state. The spectrum demonstrates immaterial contribution from metallic Ru (Ru:3d5/2 = 281.98 eV). The O-1s spectrum of the Pd-Ru/CNFs electro-catalyst (**Figure 5.4(c)**) shows four binding energy peaks with respect to the overall % area of the core level at 531.67 eV, 7.5%, 532.82 eV, 51%, 534.28 eV, 39.5% and 536.37 eV, 2% which could be ascribed to C=O, C-O-H, C-O-C and O=C-O functional groups as marked in the graph. O 1s fitted with 4 Voigt-type singlets and a Shirley-type background. The synthesized CNFs are functionalized with the carboxylic acid group in view of the XPS outcomes, which concurred with the literature [42]. **Figure 4(d)** represent the high-resolution Pd3d region XPS signal for Pd-Ru/CNFs electro-catalyst. Pd 3d core level was fitted with two spin-orbit doublets of 3d5/2 and 3d3/2, isolated by a spin-orbit splitting of 5.25 eV, and a Shirley-type background. The deconvolution of the Pd 3d spectrum uncovers that the surface area of the palladium nanoparticles is made generally out of two different Pd species in the metallic state [43]. The binding energies with % area of the two components of around 335.66 eV, 33.3% which can be attributed as metallic Pd(0) and around 339.02 eV, 66.7% which can be ascribed as Pd2+, for example, palladium oxides or hydroxides [44]. The respective intensities of those two signals demonstrated that Pd0 was the standard oxidation state on the surface area of the Pd-Ru/CNFs.
Figure 5.4: XPS (a) survey spectra for Pd-Ru/CNFs (b), C 1s + Ru 3d for Pd-Ru/CNFs (c), O 1s for Pd-Ru/CNFs (d), Pd 3d for Pd-Ru/CNFs.

Table 5.1: Elemental composition of Pd-Ru/CNFs obtained from XPS data.

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<th>Sample</th>
<th>Carbon %</th>
<th>Oxygen %</th>
<th>Palladium %</th>
<th>Ruthenium %</th>
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<tr>
<td>Pd-Ru/CNFs</td>
<td>84.1</td>
<td>2.3</td>
<td>9.2</td>
<td>4.5</td>
</tr>
</tbody>
</table>
5.2.2. Electrochemical analysis of the synthesized electro-catalysts: Ethanol oxidation reaction (EOR) activity

5.2.2.1. Cyclic voltammetry

The cyclic voltammetry (CV) analysis for ethanol oxidation was performed in an alkaline medium at a sweep rate of 50 mVs\(^{-1}\) at room temperature. Figure 5.5 shows cyclic voltammograms of the Pd/C, Pd/CNFs, Pd-Ru/CNFs in 1M ethanol (CH\(_3\)CH\(_2\)OH) and 1M KOH solutions. The Pd/CNFs and Pd-Ru/CNFs electro-catalysts show two well distinctive ethanol anodic current peaks in the forward and backward scans (Figure 5.5). The current peak formed in the forward scan is ascribed to the ethanol electro-oxidation reaction and the peak formed in the backward scan is identified with the electro-oxidation of residual carbonaceous materials [45,46]. As shown in fig.5, the ethanol oxidation current densities are 440 μA cm\(^{-2}\), 1160 μA cm\(^{-2}\), 1391 μA cm\(^{-2}\) for Pd/C, Pd/CNFs and Pd-Ru/CNFs electrocatalysts respectively. It can be observed that the Pd-Ru/CNFs electrocatalyst represents the highest current density towards ethanol electro-oxidation in alkaline conditions. The addition of RuNPs to Pd/CNFs as an electro-catalyst in alkaline media improve the electro-catalytic activity by increasing resistance towards the poisoning of the Pd catalyst surface by strongly intermediate carbonaceous material [38]. The CV results indicated that Pd-Ru/CNFs electro-catalyst shows the best catalytic activity in relation to high current density and low onset potential when contrasted with the Pd/CNFs and Pd/C electrocatalyst. As presented in fig.5, the onset potential for the prepared Pd-Ru/CNFs electrocatalyst is the lowest. The onset potentials were observed at -0.50 V, -0.50 V, -0.55 V for Pd/C, Pd/CNFs and Pd-Ru/CNFs electrocatalysts respectively. The ratio of the forward peak (\(I_f\)) to the backward peak (\(I_b\)) can be utilized to estimate the degree of poisoning tolerance of the synthesized electro-catalyst [47]. The ratios (\(I_f/I_b\)) are calculated to be 1.4, 1.5 and 1.6 for the Pd/C, Pd/CNFs and Pd-Ru/CNFs electrocatalysts indicating that the Pd-Ru/CNFs has the highest poisoning tolerance. This behaviour is dependent on the atomic concentration of the Pd, Ru and C on the surface of the nanoparticles as obtained from XPS data (see table 5.1).
5.2.3. Electrochemical analysis of the synthesized electro-catalysts: Methanol oxidation reaction (MOR) activity

5.2.3.1. Cyclic voltammetry

The methanol oxidation activity of the Pd-Ru/CNFs electro-catalyst was tested in 1M methanol (CH₃OH) and 1M KOH electrolyte at a sweep rate of 50 mVs⁻¹ at 298 K. The methanol electro-oxidation was evidently observed in Figure 5.6, demonstrating two well-defined peaks in the forward and backward sweep. The magnitude of the signal current in the forward sweep shows the catalytic activity of the catalyst towards the methanol oxidation reaction and the reverse sweep is related with the expulsion of the residual carbon species formed in the positive sweep in alkaline medium [48,49]. As shown in Figure 5.6, the onset potential of Pd-Ru/CNFs is lower as contrasted with the of the Pd/CNFs and commercial Pd/C electro-catalysts. The anodic current densities were observed at 624 µA cm⁻², 1212 µA cm⁻² and 1383 µA cm⁻² for the Pd/C, Pd/CNFs and Pd-Ru/CNFs electro-catalysts, respectively.
respectively. From the CV results, it is noticeable that the Pd-Ru/CNFs electro-catalyst shows better catalytic activity towards methanol electro-oxidation in alkaline conditions. The introduction of Ru NPs into the Pd/CNFs electro-catalyst lowers the oxidation peak potential from -1.2V to -1.9V. The ratio of the forward anodic peak current to the backward anodic peak current \( (I_f/I_b) \) can be utilized to portray the contamination tolerance of the electro-catalysts [50]. The ratio \( (I_f/I_b) \) was calculated to be 1.4, 1.5 and 1.6 for the Pd/C, Pd/CNFs and Pd-Ru/CNFs electrocatalysts. A high \( (I_f/I_b) \) ratio shows a small amount of the carbonaceous intermediates build up on the surface of the electro-catalyst due to good methanol oxidation reaction during the forward sweep and a low \( (I_f/I_b) \) value demonstrate the converse case [51]. It has been reported that higher current densities for the Pd-Ru/C electro-catalyst towards electro-oxidation of alcohol in alkaline media were also observed by Awasthi et al.[22] and Bambagioni et al.[26], but less than our synthesized Pd-Ru/CNFs electro-catalyst.
Figure 5.6: Cyclic voltammetry graphs of Pd/C, Pd/CNFs, and Pd-Ru/CNFs electro-catalysts in 1.0 M KOH + 1.0 M CH₃OH solution at a scan rate of 50 mVs⁻¹ at room temperature.

5.2.4. The effect of scan rate on the current density

Since Pd-Ru/CNFs performed better than other electro-catalysts prepared in terms of high current density, poisoning tolerance and low onset potential, then further studies were carried out using this electro-catalyst. Figure 5.7 represent the cyclic voltammograms of electro-oxidation of ethanol in 1M EtOH and 1M KOH solutions on Pd-Ru/CNFs electro-catalyst at different scan rate (20-100 mVs⁻¹). As depicted in the Figure 5.7(a), as the scan increases, the anodic peak current occurs at higher peak potentials. The current density of the anodic peak increases by increasing the scan rate. The relationship between the peak current density and the sweep rate studies are shown in the Figure 5.7(b), which means current density is directly proportional to the scan rate.

![Cyclic Voltammograms](image)

Figure 5.7: Cyclic Voltammograms of Pd-Ru/CNFs on GC electrodes in 1.0 M KOH + 1.0 M CH₃CH₂OH at different scan rates (a) and the plot of peak current density vs. scan rates studies (b).

Figure 5.8(a) illustrates the cyclic voltammograms of methanol oxidation in 1M CH₃OH and 1M KOH solutions on Pd-Ru/CNFs electrode at different scan rates (20-100 mVs⁻¹) while figure 5.8b, represent the relationship between current...
density acquired from forward sweep vs \( v/V_s \). As shown in Figure 5.8(b), that as the sweep rate is increased the anodic peak current density increases. Hence the current density is linearly proportionally to the sweep rate, which implies that the methanol oxidation on Pd-Ru/CNFs electro-catalyst on the electrode might be controlled by a diffusion process [52,53].

**Figure 5.8**: Cyclic Voltammograms of Pd-Ru/CNFs on GC electrodes in 1.0 M KOH + 1.0 M CH₃OH at different scan rates (a) and the plots of peak current density vs. scan rates studies (b).

### 5.2.5. Electrochemical analysis of the synthesized electro-catalysts: EOR activity

#### 5.2.5.1 Chronoamperometry studies in ethanol electro-oxidation

Chronoamperometry measurements were carried out to assess the long-term poisoning rates/stability of the electro-catalysts. The chronoamperograms of the three prepared electro-catalysts in a solution of 1M EtOH + 1M KOH at a steady potential-0.2 V vs Ag/AgCl after the 2000s are displayed in Figure 5.9. The current density acquired for commercial palladium supported on activated carbon (Pd/C) is significantly lower compared to the other two electro-catalysts for the duration of operation (the 2000s). The Pd-Ru/CNFs electro-catalyst represents better long-term stability and higher poisoning tolerance followed by Pd/CNFs and Pd/C electro-catalyst towards ethanol oxidation in alkaline conditions. These results
reveal that the addition of Ru hinders Pd/CNFs from leaching, producing higher stability to Pd/CNFs electro-catalyst and enhance electro-catalytic activity towards ethanol oxidation reaction [54,55].

Figure 5.9: Chronoamperometry of Pd/C, Pd/CNFs and Pd-Ru/CNFs electro-catalysts in 1.0 M KOH + 1.0 M CH₃CH₂OH.

5.2.6. Electrochemical analysis of the synthesized electro-catalysts: MOR activity

5.2.6.1 Chronoamperometry studies in methanol electro-oxidation

The electrocatalytic stability of Pd/C, Pd/CNFs and Pd-Ru/CNFs modified GC electrodes towards methanol oxidation in alkaline media was investigated using Chronoamperometry. In Figure 5.10 chronoamperometric curves represent the long-term stability and higher poisoning tolerance of the three palladium electro-catalysts in 1M EtOH + 1M KOH solutions under applied potential for 2000s. The current density obtained from the Pd-Ru/CNFs electro-catalyst was 2 times higher as compared to Pd/CNFs and Pd/C electro-catalysts. The current density of the
Pd-Ru/CNFs electro-catalyst remained higher for the duration of the measurement showing higher poisoning tolerance and stability than the Pd/CNFs and Pd/C electro-catalysts. These results confirm that the addition of Ru nanoparticles produces surface oxygen-containing species that bonds with the strongly carbonaceous intermediates, as improved poisoning stability was observed for the prepared Pd-Ru/CNFs electro-catalyst [56,57].

Figure 5.10: Chronoamperometry of Pd/C, Pd/CNFs and Pd-Ru/CNFs electro-catalysts in 1 M KOH + 1 M CH₃OH.

5.2.7. Electrochemical impedance study

Electrochemical impedance spectroscopy (EIS) was utilized to assess the ethanol and methanol oxidation kinetics on the binary and ternary composite electrodes in alkaline medium. The impedance study of the three palladium electro-catalysts, namely Pd/C, Pd/CNFs and Pd-Ru/CNFs was conducted in the frequency range of 0.01 - 10 x 10³ Hz at a consistent dc potential, 0.2 V vs RHE in 1 M KOH + 1 M (EtOH & MetOH) and the results are displayed in Figure 5.11 (a, b). All the EIS
spectra appeared in Figure 5.11 (a, b) seem to be comparative. The electrical proportional circuit model, Rs-solution resistance and Rct-charge transfer resistance was utilized to reproduce the test information of the present anode electrolyte system [58]. The electro-catalyst with little palladium nanoparticles (Pd-Ru/CNFs) had the most minimal Rct values at 0.2 V, which is in concurrence with the higher mass activities seen in both cyclic voltammetry and chronoamperometric studies. The electro-catalysts with large palladium nanoparticles had significantly larger impedance arcs, indicating slower ethanol and methanol oxidation kinetics. The electro-catalyst with vast palladium nanoparticles had significantly bigger impedance arcs, demonstrating slower ethanol and methanol oxidation kinetics [59]. This binds in with the lower mass activities acquired in both cyclic voltammetry and chronoamperometric measurements for these electro-catalysts. For the electro-catalyst with huge palladium particles, a low-capacitive loop was detected [60]. This can be ascribed to an expansion in OH\textsubscript{ad} sites at the higher potential which oxidizes the adsorbed intermediates, along these lines authorizing the metal destinations to facilitate oxidation [61]. From the Nyquist plots, ethanol and methanol oxidation is usually denoted by frequency inductive loop with a diameter representing charge transfer resistance (Rct) [62,63]. The Rct value is relatively large for commercial Pd/C, medium for Pd/CNFs and small for Pd-Ru/CNFs suggesting that Pd/C has a slowest electro-transfer kinetics while Pd/CNFs has the fastest electron transfer kinetics following Pd-Ru/CNFs electro-catalyst. Figure 5.11(a, b) demonstrates that the diameter of the semi-circle diminishes with the addition of Ru nanoparticles in the composite material. Also, it is depicted in Table 1 that the introduction of Ru nanoparticles diminishes the Rct significantly and hence enhances the rate for HER process. The Pd-Ru/CNFs electro-catalyst is the best dynamic among the series. Precisely, a similar conclusion has likewise been observed from the CV study.
Figure 5.11: Impedance plots of Pd/C, Pd/CNFs and Pd-Ru/CNFs catalysts on GC electrode in (a) 1 M KOH + 1 M CH$_3$CH$_2$OH (b) 1 M KOH + 1 M CH$_3$OH solution with equivalent circuit used in the fitting of the electrochemical impedance spectra.

The circuit parameters were derived from Figure 5.11 and compared in Table 5.2 bellows.

**Table 5.2**: Circuit parameters for ethanol and methanol electro-catalysts.

<table>
<thead>
<tr>
<th>Electro-catalysts</th>
<th>Ethanol</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_s$/Ohm</td>
<td>$R_{ct}$/Ohm</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.884</td>
<td>21.28</td>
</tr>
<tr>
<td>Pd/CNFs</td>
<td>0.526</td>
<td>15.53</td>
</tr>
<tr>
<td>Pd-Ru/CNFs</td>
<td>0.376</td>
<td>11.20</td>
</tr>
</tbody>
</table>
References


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Chapter 5: Results and discussions.


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6.1. Conclusion

The aim of this work was to explore the effect of carbon nanofibers (CNFs) as supports for Pd based catalysts (Pd/CNFs and Pd-Ru/CNFs) on direct alcohol fuel cell (DAFC) in alkaline medium. And commercial Pd/C was used as the reference. This aim was achieved by synthesizing CNFs, Pd/CNFs, Pd-Ru/CNFs to mitigate the overall cost of the supported electro-catalyst and enhance the CO poisoning tolerance of the electro-catalysts. Highly functionalised carbon nanofibers were successfully prepared using a simple and cheap green method. Structural attributes of the synthesized electro-catalysts were evaluated using FTIR, Raman spectroscopy, TEM, SEM, XRD and XPS. The activity, stability and conductivity of the electro-catalyst were tested using CV, CA and EIS.

In Chapter 4, the Pd/CNFs electro-catalyst was successfully prepared using alcohol reduction method.

1. The FTIR studies showed peaks which correspond to carboxylic acid functional groups. These results confirmed that carboxylic acid functional groups were indeed incorporated onto the surface of the CNFs material.

2. The Raman results demonstrated similar intensity ratio ID/IG of 0.91 showing similar structural defects between disordered carbon peak (D) and graphite peak (G) on the CNFs.

3. The TEM image of Pd/CNFs electro-catalyst displayed a successful attachment of palladium nanoparticles onto the surface of the carbon nanofibers, proposing an electrostatic interaction between Pd nanoparticles and the carboxylic group of CNFs.
4. The XRD results revealed that the structure of Pd/CNFs was polycrystalline palladium consisted of defective graphitic crystal lattice. 5. XPS analysis revealed the composition of the nanomaterials and the oxidation states of Pd onto the surface layers of Pd/CNFs composite material.

6. The cyclic voltammetry studies confirmed that the Pd/CNFs electro-catalyst exhibited high catalytic activity compared to the commercial Pd/C electro-catalyst in both ethanol and methanol electro-oxidation in alkaline conditions.

7. Chronoamperometry tests prove that the Pd/CNFs electro-catalyst has a better long-term stability and lower poisoning rate than commercial Pd/C electro-catalyst.

In chapter 5, the Pd-Ru/CNFs electro-catalyst was successfully prepared using alcohol reduction method.

1. The SEM elemental mapping analysis confirmed the presence of the Pd, Ru, C and O elements on the surface of Pd-Ru-CNFs electro-catalyst. The dispersion of Pd and Ru match well, indicating the successful synthesis of a composite material and the full attachment between Pd and Ru phases. Carbon is well dispersed over the whole of CNFs and the small amounts of oxygen are detected.

2. XRD results confirmed that the addition of Ru to Pd/CNFs electro-catalyst shifts the peaks to higher 2θ values. The diffraction peaks observed for the Pd-Ru/CNFs electro-catalyst are wider than that of Pd/CNFs showing a reduction in particle size and increment in the lattice parameter of palladium. Furthermore, there are no diffraction planes related to Ru implying that Ru is highly alloyed to palladium structure, resulting in improved activity of the Pd-Ru/CNFs electro-catalyst.

3. XPS results showed that incorporating Ru in the Pd/CNFs electro-catalyst shifts the binding energy peaks positively indicating a strong electrostatic interaction of the metal support.
4. During cyclic voltammetry studies, the synthesized Pd-Ru/CNFs electro-catalyst represent the higher current density towards ethanol and methanol electro-oxidation in alkaline media. The onset potential of Pd-Ru/CNFs electro-catalyst is lower as compared to that of the Pd/CNFs and commercial Pd/C electro-catalysts demonstrating better electro-catalytic activity. A linear relationship was observed for the Pd-Ru/CNFs electro-catalyst from the plot of peak current density (IP) against the sweep rate (v/Vs⁻¹) showing that the methanol electro-oxidation reaction in alkaline media is a diffusion-controlled process.

5. The chronoamperometric study was performed and it was observed that the current decay of the Pd-Ru/CNFs electro-catalyst is slower than that of Pd/CNFs and commercial Pd/C electro-catalysts indicating higher poisoning tolerance and better long-term stability. These results confirm that the addition of Ru nanoparticles to Pd/CNFs composite material produces surface oxygen-containing species that bonds with the strongly carbonaceous intermediates.

6. EIS also showed that Pd-Ru/CNFs electro-catalyst has the better conductivity with a decrease in Rct hence the fastest electro-transfer kinetics.

7. In conclusion the addition of Ru nanoparticles to Pd/CNFs composite material improve the electro-catalytic activity by increasing resistance towards the poisoning of the Pd catalyst surface by strongly intermediate carbonaceous material. The Pd-Ru/CNFs electro-catalyst showed a higher performance towards methanol oxidation as compared to ethanol oxidation in alkaline media. This could be because of the need of dissociative chemisorption of ethanol molecule throughout electro-oxidation reactions in which adsorption of strongly carbonaceous intermediates may take place.

6.2. Recommendations for further work

This study recommends that the synthesized electro-catalyst supported on carbon nanofibers should be used as anode catalyst towards the commercialization of direct methanol fuel cells as they demonstrate both activity and durability. Even though CNFs
Based electro-catalysts indicate extremely encouraging outcomes, additionally studies should be conducted. In-situ FTIR measurements would be useful in the comprehension of the reaction mechanism of methanol and ethanol oxidation in alkaline conditions. These electro-catalysts need to be tested towards glycerol and ethylene glycol oxidation in alkaline media and assess the rate of catalytic poisoning. Further improvement in CO resistance could be accomplished by the addition of a third metal, Ni, Sn or Co.