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Chapter

Electrochemical Investigation of Heat Treated PtRu Nanoparticles Prepared by Modified Polyol Method for Direct Methanol Fuel Cell Application

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Abstract

In this work, heat-treated PtRu metal alloys based on multi-walled carbon nanotubes (MWCNT) were synthesized using modified polyol approach for methanol oxidation reaction (MOR) in acidic conditions at 2500, 3500, and 4500 C. The catalysts physical and electrochemical properties were investigated. The High Resolution Transmission Electron Microscopy (HR-TEM) was used to determine the shape, particle size, and particle size distribution of the catalysts, where spherical and agglomerated PtRu nanoparticles with narrow particle size distribution were observed with particle sizes ranging from 0.600 to 1.005 nm. Their crystalline sizes were assessed using the XRD with catalysts presenting a face-centered crystal structure, which is typical of platinum structures with crystalline sizes ranging from 0.500 to 1.180 nm. Energy-Dispersive Spectroscopy, (EDS), was used to identify the elements. Cyclic voltammetry (CV) was used to determine the electroactive surface area (ECSA) and MOR of the electrocatalysts, whereas electrochemical impedance spectrometry (EIS) and chronoamperometry (CA) were used to study their electro-kinetics and stability towards MOR, respectively. PtRu/MWCNT electrocatalysts alloyed at 450°C showed better electroactivity and kinetics as compared to other catalysts, evident from the highest current density of 19.872 mA/cm^2 and lowest charge transfer resistance of $0.151 \text{ k}\Omega$ from CA and EIS, respectively.

Keywords: methanol oxidation, catalysts, multi-walled carbon nanotubes, heat treatment, electroactivity

1. Introduction

A device called a fuel cell produces electricity through chemical processes. The cell can continue to generate power as long as fuel is available [1, 2]. In order to provide sustainable electricity, fuel cells combine well with other clean, contemporary
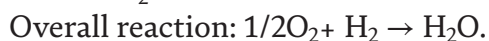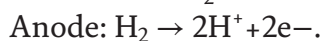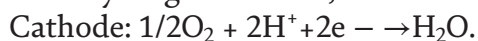
energy sources including wind, solar, and hydroelectricity. These devices have a variety of uses in portable devices, stationary equipment, and transportation, as well as silent operation without vibration and inherent modularity that enables simple design [3].

The versatile and mutual conversion of chemical to electrical energy via fuel cell technologies has been considered a green approach and environmentally friendly than the combustion of fossil fuels. The combustion of fossil fuel to generate energy has contributed to acid rain, ozone depletion and climate change. Furthermore, this is as a result of air pollution and harmful greenhouse gases such as $CO2$ [2, 4]. The Kyoto Protocol has since then suggested the use of renewable energy sources, the promotion of existing high efficiency electricity technologies, and the adoption of advanced low-$CO2$ emission energy systems [2, 5], there has been intensive research and development of renewable and environmentally friendly ways to generate electricity.

Electrochemical systems, such as fuel cells, effectively transform chemical energy directly into electricity, with water and heat as byproducts [3]. The device is composed of four major components: anode and cathode electrodes, an electrolyte, and a gas diffusion layer. The anode electrode of the device receives fuel, whereas the cathode electrode receives oxygen or air. The basic objective of an electrolyte located between the electrodes, regardless of the type of cell, is always to move ions (anions or cations) from one side to the other [6].

In the early 1800s, Sir William Grove reported the first fuel cell when he built the gas battery, a device that combined hydrogen and oxygen to produce electricity. This technology was later referred to as a fuel cell. Francis Thomas Bacon demonstrated the first fully working fuel cell in 1959 [3, 4]. There are various varieties of fuel cells accessible today, each having its unique chemical fuel input and operating principles (**Figure 1**).

For a hydrogen fuel cell, similar cathode and anode reactions are

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

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

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

1.1 Fuel cells technologies

The choice of an electrolyte used in fuel cells is the most significant factor and gives it an identity. The operating conditions such as temperature range, catalyst desired, type of fuel, and other parameters have an effect on the electrochemical processes taking place in the cell due to the distinction of electrolytes [8]. Thus qualities influence the applications for which these cells are best suited. Various fuel cell types are now being explored, each with their own set of advantages, limitations, and prospective applications [8]. PEMFCs, direct methanol fuel cells, alkaline fuel cells, phosphoric acid fuel cells, solid oxide fuel cells, and molten carbonate fuel cells are all examples of fuel cells.

1.2 Catalyst

A catalyst helps to speed up a chemical reaction by creating bonds with the molecules involved. The catalyst permits the reactants to react to produce a product, which then detaches from the catalyst and leaves it undamaged for the next reaction. As a result, a catalytic reaction may be thought of as a cyclic event in which the catalyst precipitates and then returns to its original state at the conclusion of the cycle.
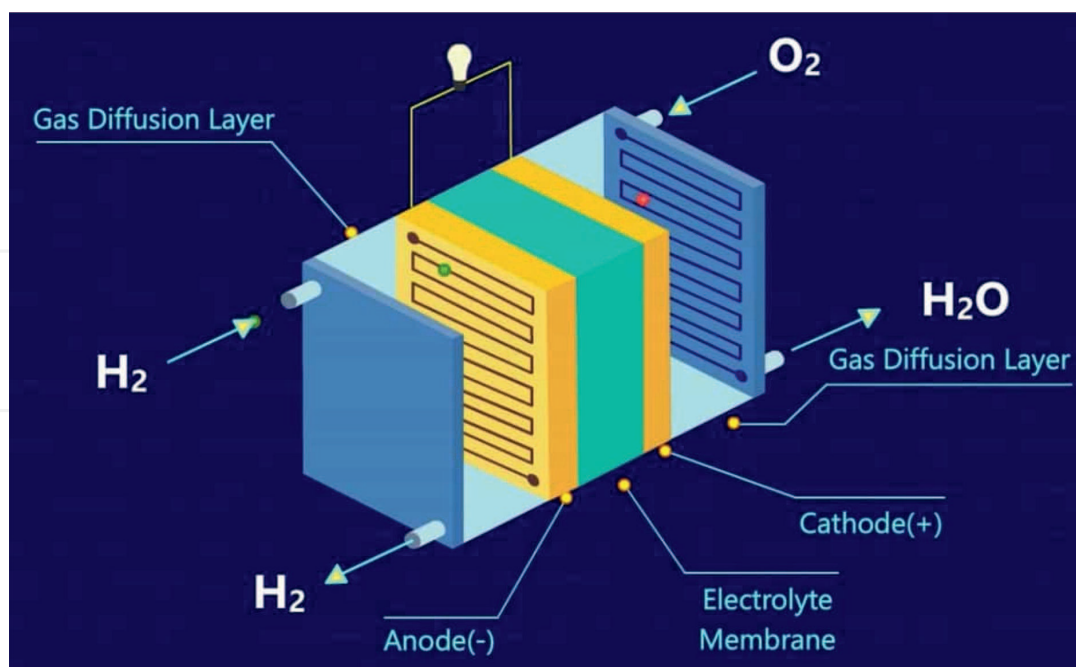
Figure 1.
A schematic diagram showing a hydrogen based fuel cell [7].

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

1.3 Fuel cell electrocatalysts

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

1.4 Methanol oxidation anode catalysts

Pt, Pd, and Au are well-known precious metals that can be used as methanol oxidation catalysts in DMFCs [9–12]. As a result, these precious metal catalysts have received a lot of attention in DMFCs [9–11]. Saving money and increasing methanol oxidation activity are both appealing characteristics. The morphological variations in particle size distribution, shape, and surface structure of precious metal catalysts have a strong influence on their methanol oxidation activity [10]. Many teams have recently created better morphologies of noble metal catalysts to promote methanol oxidation activity with low metal loading [10, 11]. Platinum-based catalysts have been shown to be reactive and stable in the acidic DMFC environment [12, 13].

Another significant barrier to efficient methanol fuel-to-electric-current conversion in a DMFC is the anode catalyst's poor MOR kinetics. Surface poisoning

by chemical intermediates such as COads-like species formed during the stepwise dehydrogenation of methanol is primarily responsible for this delay [14–16].

The importance of DMFC's low efficiency and overpotential stems from oxidized adsorbed COads-like species and other poisoning intermediates for probable MOR on Pt at such potentials [17]. PtRu [18, 19], PtSn [20, 21], PdNi [22], PtMo [23, 24], PtTiO2 [25, 26], PtW [23], PtOs [27], and PtMn [28] are examples of binary Pt-based alloy (double-component) catalysts. The concept of metal alloys is to enhance methanol electro-oxidation activity, by supplying a flux of hydroxyl species to negative electrode at higher potentials to facilitate the reaction with COads-like poisoning species. The methanol oxidation and associated mechanisms have been studied under controlled conditions in a variety of catalytic systems [29–37].

Platinum's electroactivity appears to be influenced by its morphology [38], with roughened platinum having significantly higher activity [39].

Several researchers have looked into the effect of particle size on methanol oxidation [40–42]. For particles with a diameter of less than 5 nm, several scientists have found a decline in activity as the particle size decreases [43–46].

On a pristine platinum electrode, linearly bound CO can cover up to 90% of the active sites, blocking the majority of them. These findings have been frequently confirmed by various researchers [47–49].

Platinum has been looked at a lot as an electrocatalyst for the oxidation of methanol. To remain being active it is used as a composite to avoid formation of CO. This has led to the search for other active materials, especially those that could work with platinum as a promoter by making it easier for chemisorbed CO to be oxidized [13].

Ru has been discovered to enhance anti-poisoning effectiveness. The Pt-Ru catalyst's high price, however, is one of the main obstacles to its broad implementation [50]. Reduced catalyst costs are a key factor in the widespread commercialization of DMFCs [51]. A number of organizations have worked diligently to create new multi-component catalyst systems for the oxidation of methanol, including PtRuNi [52–54], Pt–Ru–Os [55, 56], Pt–Ru–Mo–W [56] and Pt–Ru–Sn–W [57]. Investigations on the Pt-Ru-Sn system were also conducted [58], but it was found that adding tin to the Pt-Ru alloy causes the Ru to be evacuated with minimal advantage [59].

Fuel cells have received a lot of attention among other energy technologies due to their high rates of energy conversion, cheap availability to fuel, and environmental friendliness [60, 61].

Fuel cells use redox processes involving oxygen and fuels to turn chemical energy into electrical energy [62, 63]. Despite years of hard work, there are still certain fundamental concerns that must be addressed. Platinum is now the most popular MOR catalyst, and significant efforts have been undertaken to increase its activity and utilization. One of the numerous disadvantages of pt-based catalysts is that they are sensitive to impurities and pricey. The main methodology used in this work was alloying platinum with ruthenium metal via the modified polyol method of catalyst synthesis, and the resultant nanoparticles were subsequently heated at higher temperatures to improve the methanol electrooxidation reaction [64–66].

Because heat treatment has been shown to affect the activity of electrocatalysts, it is known as thermal activation. Heat treatment of Pt-based catalysts can result in particle-size increase, improved alloying, and changes in the surface morphology of the catalyst from amorphous nature to more crystallite phases, all of which have a significant impact on their electroactivity and stability [67].

Numerous studies [67] have been conducted to determine how heat treatment affects Pt catalysts. In this study, heat treatments of 2500C, 3500C, and 4500C are applied to binary PtRu/MWCNT catalysts made using the modified polyol method to see how they affect their shape, particle size, electroactivity, and stability towards methanol electrooxidation.

According to Valisi et al. [68], enhancing the electrocatalytic activity and stability of fuel cells, thermal treatment of catalysts plays an integral part of ORR. The ORR activity was found to be maximal as indicated, Pt/C (T, 350°C) < Pt-Co/C (T, 250°C) < Pt-Ni/C (T, 350°C) < Pt-Fe/C (T, 350°C) < Pt-Cu/C (T, 350°C).

Xiowel et al. [69] produced carbon-supported Au-PtRu catalysts for DMFC by easily depositing Au metal on top of a commercial PtRu/C catalyst and then heating it at three different temperatures. After a straightforward Au particle deposition on a commercial Pt-Ru/C catalyst, the resulting composite catalyst was heated at 125, 175 and 200 degrees Celsius in a N environment. It was discovered that among heat-treated catalysts, Au-PtRu/C catalysts had the greatest electrocatalytic stability.

Another study [70] found that heat treatment enhanced the electrical conductivity of the electrode, which influenced the agglomeration of Pt particles. Furthermore, the PtM/C alloying degree (M denotes Cr, Pd, Co) was greatly enhanced. Finally, the PEM fuel cell displayed an appealing performance, with PtCo/C delivering an approximate current density of 392.8 mA/Cm^2.

The elimination of any undesired contaminants that may have resulted from the early phases of preparation is one of the benefits of heat treatment. Heat treatment increases the electrocatalytic activity of the produced catalyst by allowing for uniform dispersion and stable metal distribution on the substrate [71, 72]. Metal particle size and distribution, particle surface morphology, and metal dispersion on the support are all affected by heat treatment. The activity and durability can be achieved from the thermal treatment subsequent to the development of Pt nanoparticles and its alloys [72]. Another study reported, Jalan et al. [73], that thermal treatment of Pt catalyst can slow down the dissolution rate and eventually decrease the initial surface area. The thermal treatment also affects the fundamental characteristics of the catalyst and its support, whereby the number of catalytic sites, the dispersion of catalyst particle on the support, the ratio of catalyst on the support, as well as the acidity-basicity properties of the support [71, 72].

There are several heat treatment technologies, including oven/furnace heating, microwave heating, plasma thermal heating, and ultrasonic spray pyrolysis. The most frequent heating technology is oven/furnace. The heat treatment approach for catalysts that use carbon black as a support for the catalytic metal is known to play two important roles in stability: the loss of oxygen-rich functional groups and graphitization of the carbon support surface. The surface chemistry concerned with carbon blacks exposes new surface states on carbon surfaces with variable oxygen-dominated functionalities that influences the chemical behavior on the surface of carbon support [74].

Firstly, the carbon black (Vulcan XC72R)-supported on Pd-V electrocatalysts were subjected to thermal treatment in 10% H2 under Ar atmosphere at a variety of temperatures. The morphological features of the heat-treated particle were studied, and it was discovered that particle size grew with increasing temperature. Heat treatment was also found to boost the electrocatalytic activity of the catalyst [75].

2. Methodology

2.1 Preparation of binary catalyst PtRu/MWCNT

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

2.1.1 Modified polyol method

Catalysts were synthesized using the processes described by Jeng et al. [76] and L. Khotseng et al. [77] for the production of platinum-based binary catalysts, with minor modifications. Ethylene glycol (EG), which works as both a reducing agent and a stabilizer [78], was chosen due to its inherent benefits, which include homogenous distribution and tiny particle size [78, 79].

In a 1:1 ratio, 75 mg of MWCNTs were mixed with 60 ml of ethylene glycol (EG). The mixture was sonicated for 15 minutes and combined at room temperature for 30 minutes to create a homogenous paste. PtRu (1,2 atomic ratio) was synthesized in a separate beaker by adding and dissolving 0.0772 mmol of H2PtCl6H2O as Pt and Ru precursor salts, respectively, in a 3:1 ethylene glycol ratio and stirring at room temperature to obtain a homogeneous mixture. The MWCNT/EG paste was mixed with salt/EG solution to adjust the pH until it reached approximately 3.6 by adding dropwise fraction amounts of 4 M NaOH. To help the metal salts adhere to the surface of the MWCNTs, the resulting mixture was subjected to an hour of vigorous stirring at high speed. The mixture was then refluxed at 160°C for three hours with a constant nitrogen flow, after which it was allowed to cool before being rinsed with ultra-pure
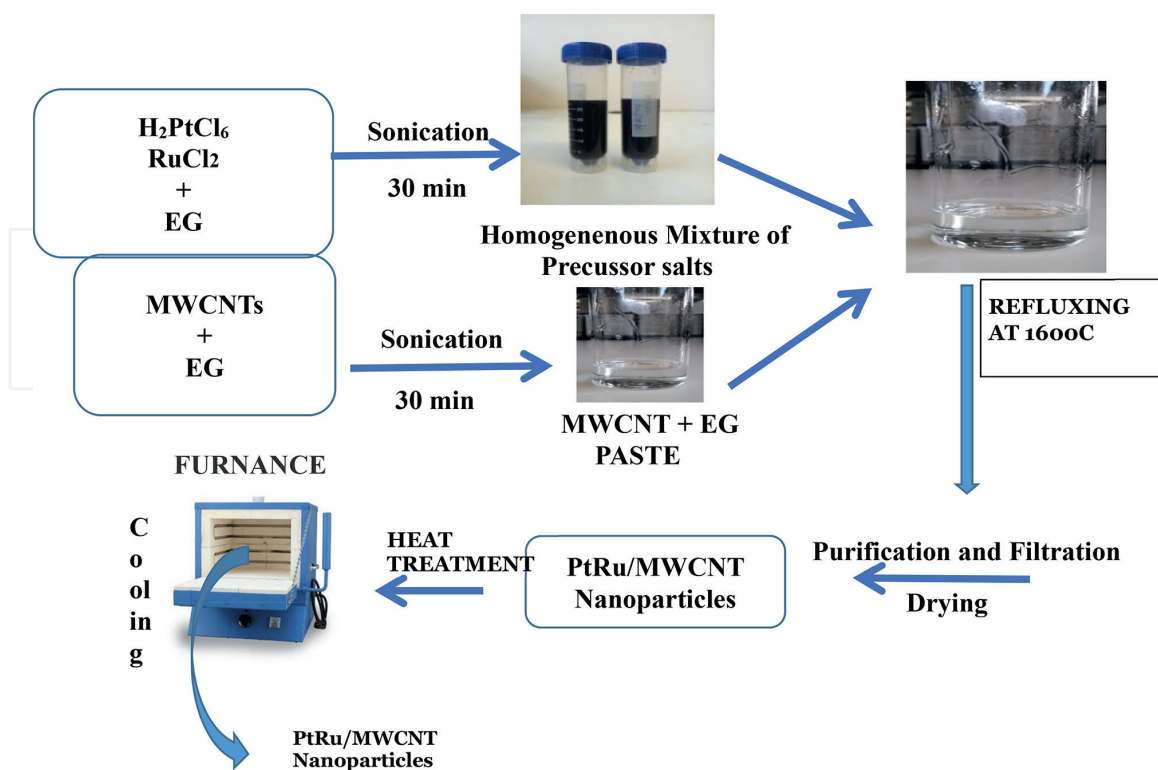

Figure 2.
Schematic diagram for the heat treated PtRu/MWCNT produced by modified polyol method of catalyst preparation.

water. Finally, the mixture was filtered, and the remaining material (PtRu/MWCNT nanoparticle) was oven-dried at 60°C for an extended period of time to produce PtRu/MWCNT catalyst.

2.1.2 Heat treatment of the catalysts

The improved polyol technique was used to produce PtRu/MWCNT inary catalysts, which were then heated under temperature control. Heat treatment has an impact on the shape, activity, and even distribution of the catalysts on the catalytic support. The desired temperature had already been set in the tube furnace. In the middle of the tube furnace, a boat made of alumina held the catalyst. While nitrogen flowed at a rate of 5 ml/min, the catalyst was heated for 3 hours at three target temperatures of 2500C, 3500C, and 4500C. After the heating period was finished, the catalyst was taken out of the furnace and the tube was cooled while the nitrogen gas flowed continuously at a rate of 5 ml/min (**Figure 2**).

3. Results and discussion

3.1 Structural characterization of heat treated PtRu/MWCNT @450°C, PtRu/MWCNT @350°C and PtRu/MWCNT @250°C electrocatalysts

Before the electrocatalysts underwent heat treatment, the metal loading was assessed using energy-dispersive X-ray spectroscopy (EDS). The modified polyol technique was used to manufacture the binary catalyst PtRu/MWCNT, which contains 5.80 percent ruthenium and 2.35 percent platinum. The microstructure of the produced electrocatalysts was evaluated by HR-TEM and XRD, and all catalysts have equivalent atomic ratios.

Scherrer's equation was used to calculate the crystallite sizes of the electrocatalysts, and high-resolution transmission electron microscopy (HR-TEM) was used to measure the particle sizes. Using Debye-Scherrer's equation, K/Cos, where K is the Scherrer constant, = 0.9, the X-ray wavelength is 0.154 nm, and (2), the width of the diffraction peak (rad), one may determine the size of the metal particles' crystals. Using Image J, (a program created by the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation, LOCI, University of Wisconsin, Madison, WI, USA), the particle size determined by HR-TEM was obtained over various regions for each electrocatalyst (**Table 1**).

The face-centered cubic (fcc)crystalline structures are present in all PtRu/CNT electrocatalysts heat treated at 250°C, 350°C, and 450°C, with PtRu/CNT@450deg. having the smallest crystalline size, according to XRD. The X-ray diffraction (XRD) pattern of the Bragg's angles of 39.760, 46.20, 67.40, 81.30, and 85.70 correspond to (111), (200), (220), and (311) and (222), respectively, and is an exact match to the X-ray diffraction pattern of the Pt catalyst. The PtRu crystals' bimetallic architecture was affected by the heat treatment, according to the Bragg angles.

Figure 3 shows the HRTEM micrographs of PtRu electrocatalysts on MWCNT heat treated at 250°C, 350°C and 450°C respectively Catalyst nanoparticle are the dark dots. Multi-walled carbon nanotubes (MWCNTs) support are the large tube-like particles seen, with diameter of about 20 nm. The PtRu nanoparticles got more agglomerated on the MWCNT as temperature increases indicating that the heat treatment made the particles of the electrocatalyst to get more closely packed (**Figure 4**).

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

Table 1.
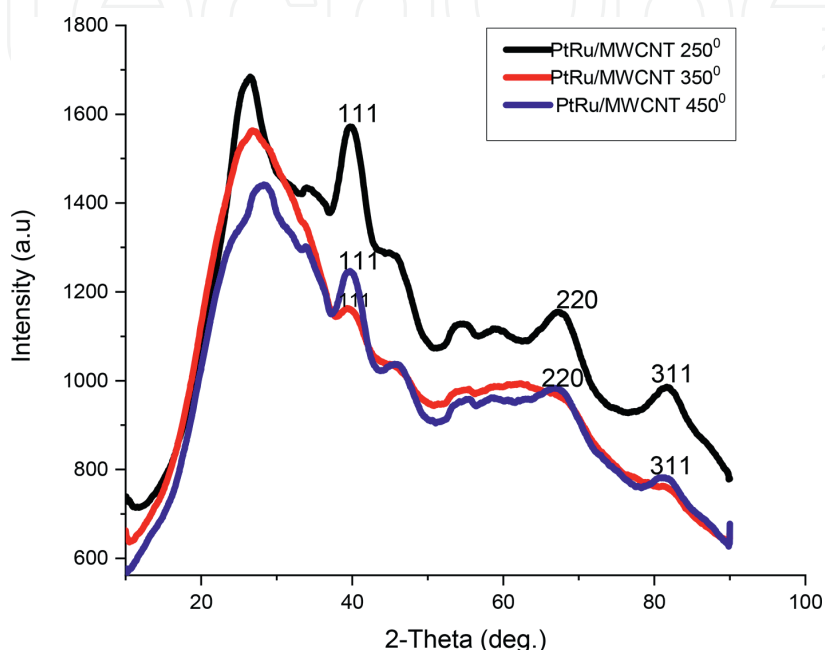*Properties of the Pt-Ru/MWCNT@ 250°C, Pt-Ru/MWCNT@ 350°C and Pt-Ru/MWCNT@ 450°C catalysts.*

Figure 3.
XRD spectra of PtRu/MWCNT@250°C, PtRu/MWCNT@350°C and PtRu/MWCNT@450°C electrocatalysts supported on MWCNTs.

3.2 Electrocatalytic activity of PtRu/MWCNT electrocatalysts at 2500, 3500, and 4500 degrees Celsius

Cyclic voltammetry was used to initially assess the electrochemical activity of the produced catalysts in a 0.5 M HClO4 solution. The adsorption peaks for the various catalysts could be seen from the cyclic voltammetry of the electrocatalysts that had been synthesized. Eq. (1) was used to calculate the electro-active surface area of the catalysts using the peak area of the adsorption peak of the electrocatalysts in cyclic voltammetry [80].

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

Ag represents the geometric surface area of the electrode (5 mm in diameter), Q represents the charge from the adsorption peak in Coulomb taking within the negative potential region −0.2 V to 0.08 V in the forward scan, and 210 Ccm-2 represents the charge of full coverage for clean polycrystalline Pt monolayer [81].
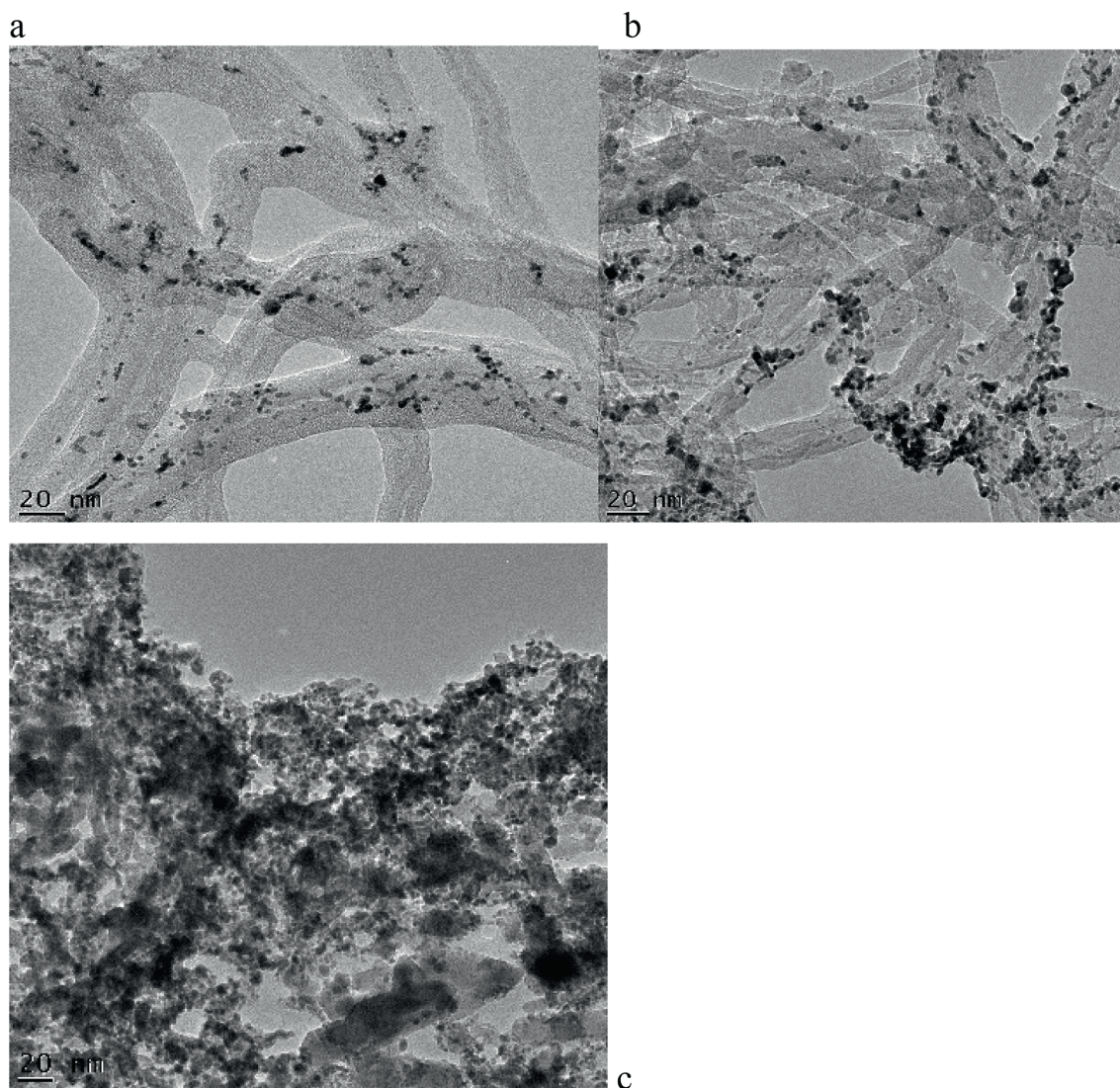
Figure 4.
HR-TEM micrographs of a) PtRu/MWCNT @250°C, b) PtRu/MWCNT @350°C) PtRu/MWCNT @450°C.

The obtained ECSA values are $16.71m^2/g$ for PtRu/MWCNT@450°C, $3.92m^2/g$ for PtRu/MWCNT@350°C and $5.098m^2/g$ for PtRu/MWCNT@250°C. Higher ECSA value of $16.710m^2/g$ for PtRu/MWCNT@450°C can be attributed to its improved alloying with lowest particle size value of 0.600 nm (**Figure 5**).

3.3 Methanol oxidation on PtRu/MWCNT@2500C, PtRu/MWCNT@3500C, and PtRu/MWCNT@4500C electrocatalysts in 0.5 M Perchloric acid solution at 30mVs⁻¹ scan rate

Table 2 summarizes the electrocatalytic activity towards methanol oxidation. By comparing the properties of the CVs, it was discovered that increasing the temperature in the metal alloys significantly increased the catalytic activity for methanol electrooxidation. To begin, the onset potentials (measures of catalytic activity) of methanol oxidation for the heat treated PtRu/MWCNT catalyst at 2500C were lower than for other electrocatalysts. The onset potential positions are as follows: PtRu/MWCNT@450°C > PtRu/MWCNT@350°C > PtRuW/MWCNT@250°C. The forward peak current densities (a measure of maximal catalyst performance) of the binary
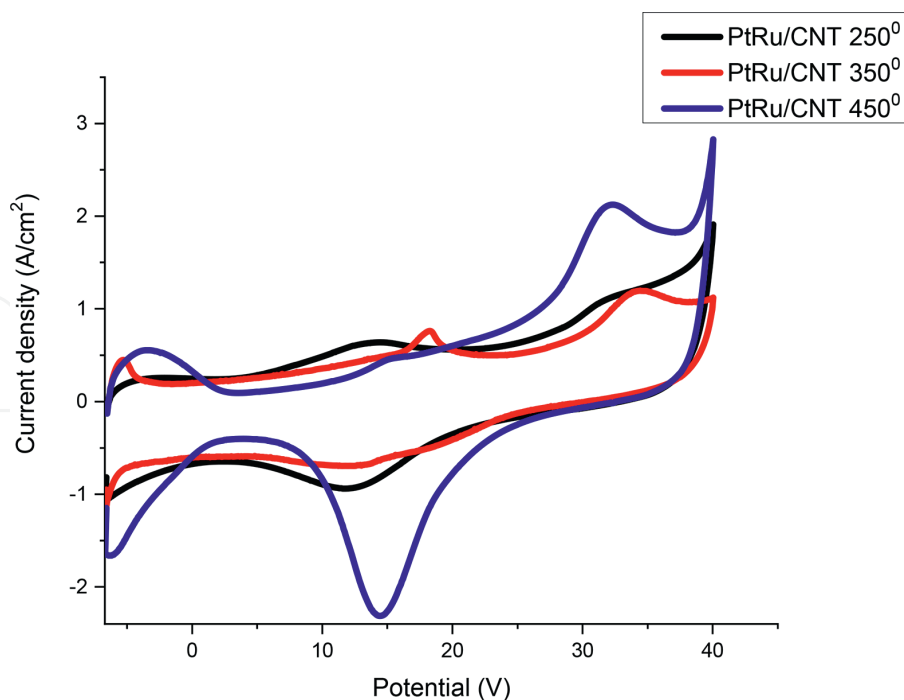
Figure 5.
Cyclic voltammograms of PtRu/MWCNT@250°C, PtRu/MWCNT@350°C and PtRu/MWCNT@450°C electrocatalysts in N_2 saturated 0.5 M Perchloric acid, $HClO_4$ at a scan rate of 30mVs^{-1}.

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

Table 2.
Comparison of the electrocatalytic activity of methanol oxidation catalysts.

catalyst PtRu/MWCNT were in the following order: PtRu/MWCNT@450°C > PtRu/MWCNT@2500C > PtRuW/MWCNT@350°C.

Thus, the binary catalyst PtRu/MWCNT@450°C exhibited best electrochemical performance in terms of the highest forward peak current density followed PtRu/MWCNT@250°C (**Figure 6**).

Several researchers thermally treated Pt-based catalysts. Valisi et al. [68] used varied temperatures to heat treat PtCo/C, PtNi/C, PtCu/C, and PtFe/C. PtCu/C at 250°C showed the highest catalytic mass activity in the research. Makodo Uchida et al. [82] used a heat-treated PtRu catalyst as well. The heat treatment is not only favored for the significant durability of the Pt-Ru catalyst in air at 370 degrees, consequently improves methanol oxidation. This process was performed at an initial overpotential of 340 mV vs. NHE at 60 mA cm^{-2}.

We report herein on heat treated bimetallic PtRu/MWCNT as given in **Table 3** below.

PtRu/MWCNT at 450°C showed better stability and kinetics towards the methanol oxidati9n reaction indicating improved electroactivities at higher heat treatment (**Figure 7**).
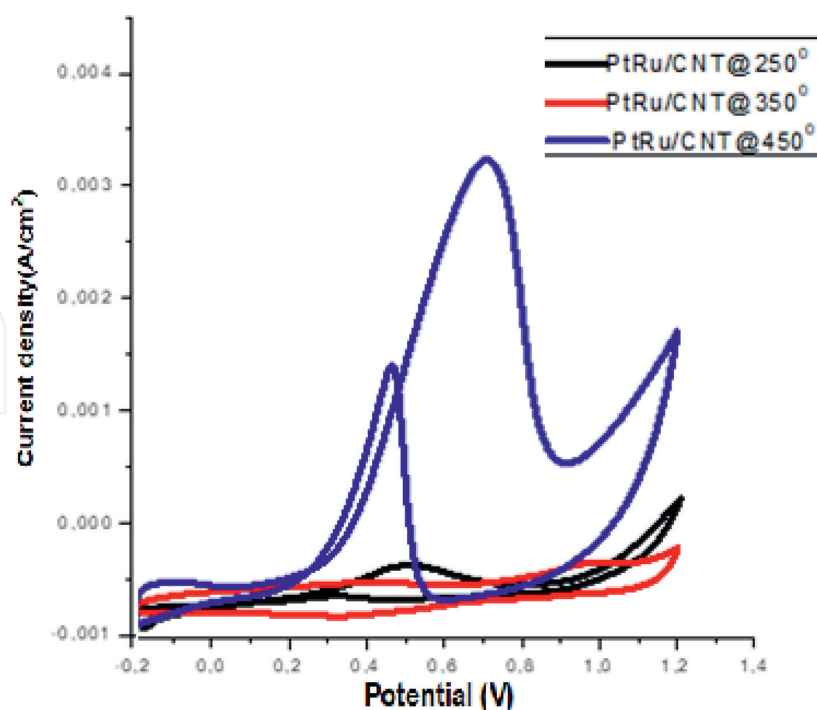
Figure 6.
Cyclic voltammograms of PtRu/MWCNT@250°C, PtRu/MWCNT@350°C and PtRu/MWCNT@450°C, purged with N_2, 2 M methanol, $HClO_4$, saturated 0.5 M Perchloric acid, at a scan rate of $30mVs^{-1}$.

Electrocatalysts	Crystalline size(nm)	Particle size(nm)	Atomic ratio determined by EDX	Mass activity $(A\,g\,-\,1\,PtRu)$
PtRu/MWCNT 250°C	1.178	1.005	Pt62.0:Ru38	13.17
PtRu/MWCNT 350°C	0.596	0.616	Pt68.13:Ru31.87	5.90
PtRu/MWCNT 450°C	0.595	0.600	Pt65.62:Ru34.38	19.48

Table 3.
Different electrocatalysts' compositions, crystalline and particle sizes, and catalytic activity.

Electrochemical impedance spectroscopy technique was used to investigate the catalytic reaction kinetics for the methanol oxidation on the anodic PtRu/MWCNT@250°C, PtRu/MWCNT@350°C and PtRu/MWCNT@250°C electrocatalysts surfaces. The charge transfer resistance, Rct values using Equivalent Circuit fitting were 0.151 kΩ, 2.04 kΩ and 11.31 kΩ for PtRu/MWCNT@450°C, PtRu/MWCNT@350°C and PtRu/MWCNT@250°C respectively indicating that PtRu/MWCNT@450°C exhibited best kinetics towards the methanol electrooxidation with the best conductivity to flow of electric current (**Tables 4** and **5**).

PtRu/MWCNT heat treated at 450^0 gave best kinetics as it offered least resistance to the flow of current with charge transfer resistance value of 0.151 kΩ followed by PtRu/MWCNT heat treated at 350°C.

PtRu/MWCNT heat treated at 450^0 gave best kinetics as it offered least resistance to the flow of current with charge transfer resistance value of 0.151 kΩ followed by PtRu/MWCNT heat treated at 350°C (**Figure 8**).

Stability is critical for electrocatalysts to be employed efficiently in DMFCs. **Figure 9** shows the chronoamperometry (CA) of PtRu/MWCNT electrocatalysts
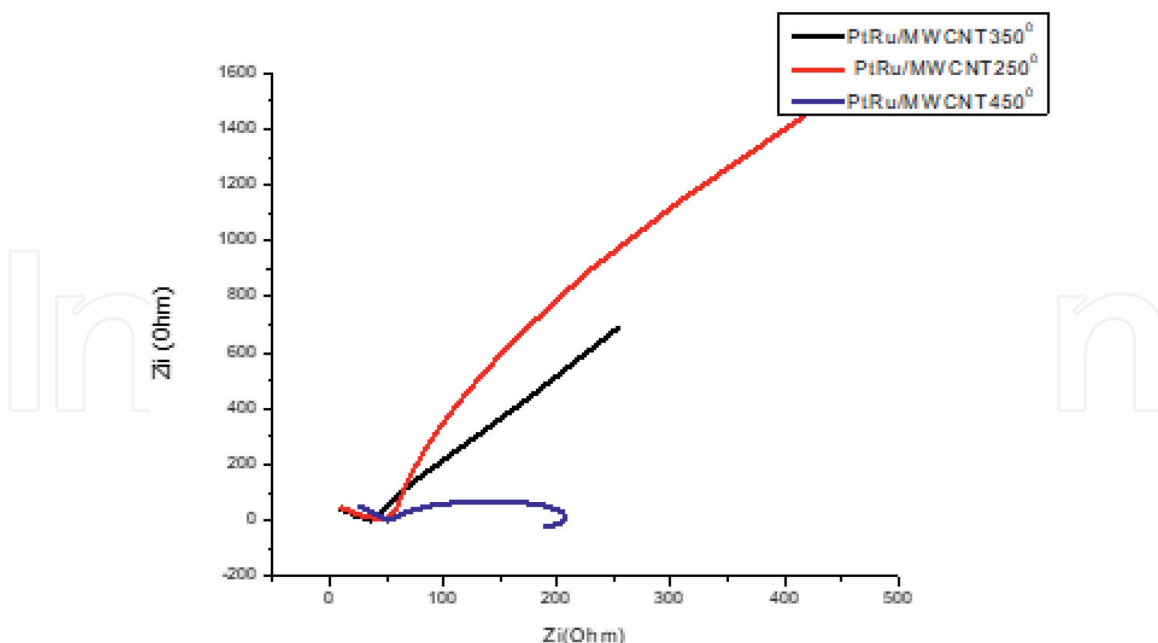
Figure 7.
EIS curves of methanol oxidation on PtRu/MWCNT electrocatalysts prepared from various synthesis routes purged with N_2 in saturated 0.5 M HClO4 and 0.2 M methanol.

Electrocatalysts	Charge transfer resistance (R_{CT})
PtRu/MWCNT 250°C	11.31 kΩ
PtRu/MWCNT 350°C	2.040 kΩ
PtRu/MWCNT 450°C	0.151 kΩ

Table 4.
Electrocatalysts with PtRu/MWCNT charge transfer resistance.

Electrocatalysts	Charge transfer resistance (R_{CT})
PtRu/MWCNT 250°C	11.31 kΩ
PtRu/MWCNT 350°C	2.040 kΩ
PtRu/MWCNT 450°C	0.151 kΩ

Table 5.
Charge transfer resistance of PtRu/MWCNT electrocatalysts.

on MWCNT support in N2 saturated 0.5 M HClO4 with 2.0 M methanol. The importance was sought after 1800 seconds on various catalysts. The current density studies were revealed on chronoamperometry analysis, an initial observation was rapid decay with time (I proportional to t-1/2). The rate of inhibition of the electrodes by the products of the methanol oxidation reaction may decrease over time. When manufactured catalysts, PtRu/MWCNT binary catalysts heat treated at different temperatures are compared, the order of stability of the electroacatalysts to methanol electrooxidation is as follows. PtRu/MWCNT at 4500C > PtRu/MWCNT at 2500C > PtRu/MWCNT at 3500C based on current density values of 0.284 mA/cm2 (**Table 6**).
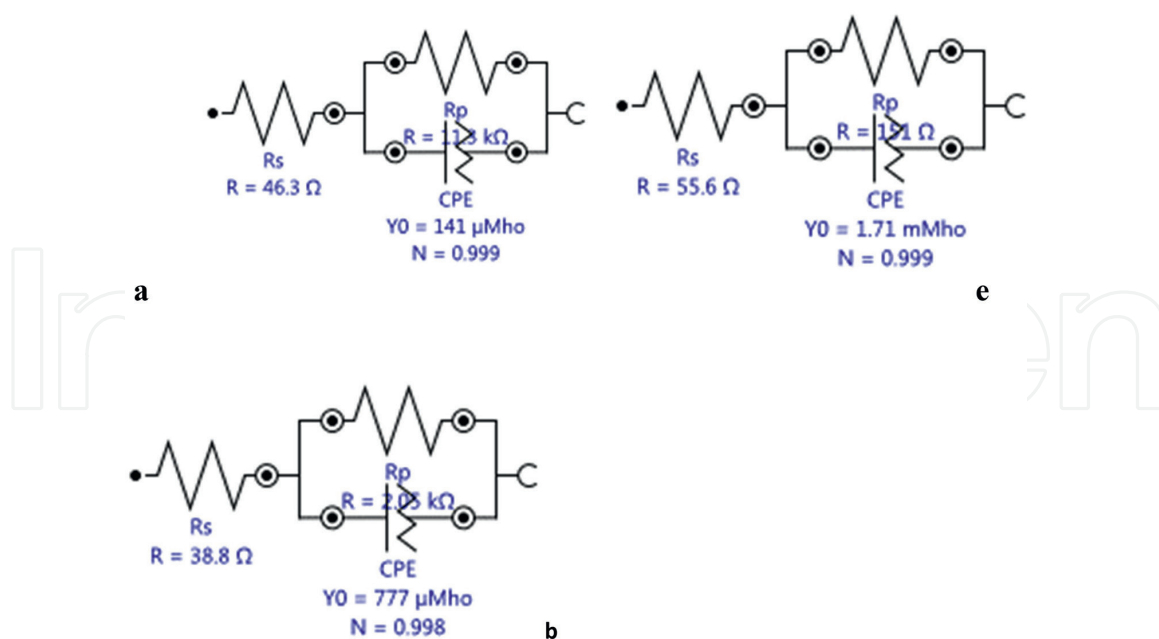
Figure 8.
Equivalent circuits for methanol oxidation electrochemical impedance spectroscopy on (a) PtRu/MWCNT@450oC, (b) PtRu/MWCNT@350oC, and (c) PtRu/MWCNT@250oC electrocatalysts in N2 saturated 0.5 M HClO4 and 0.2 M methanol.
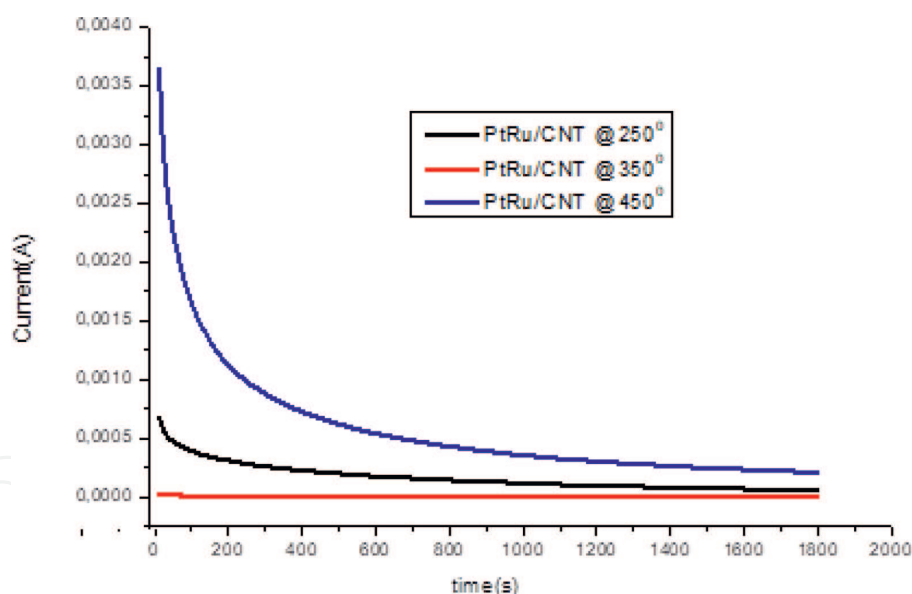

Figure 9.
The Chronoamperometry curves of methanol oxidation on PtRu/MWCNT electrocatalysts in 0.5 M HClO$_4$ and 2.0 M CH$_3$OH.

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

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

4. Conclusion

In this study, PtRu supported on MWCNT was successfully synthesized using the modified polyol approach and heat treated at 2500C. 3500 and 4500 degrees Celsius, respectively. The synthesized electrocatalysts had crystalline diameters of 0.595–1.178 nm and average particle sizes of 0.699–1.005 nm, according to XRD and HRTEM studies. The PtRu alloy phase, according to XRD studies, is an excellent match for the Pt catalyst structure. The PtRu/MWCNT electrocatalyst heat-treated at 4500 C was shown to have higher electrocatalytic activity for methanol oxidation, with a mass activity of 19.48 A/g, than other PtRu electrocatalysts on MWCNT support. When compared to other electrocatalysts, the 4500C PtRu/MWCNT electrocatalyst displayed the maximum current density for methanol oxidation. This is because it participates most actively in the anode oxidation reaction and has the lowest particle size. The PtRu/MWCNT electrocatalysts heated to 4500C showed faster electrochemical reaction kinetics than those heated to 2500C and 3500C with a charge transfer resistance value of 0.151 k Ω, according to the EIS.

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

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References

[1] O'hayre R, Cha S-W, Colella W, Prinz FB. Fuel cell fundamentals. John Wiley & Sons; 2016

[2] Elmer T, Worall M, Wu S, Riffat SB. Fuel cell technology for domestic built environment applications: State of-the-art review. Renewable and Sustainable Energy Reviews. 2015;**42**:913-931

[3] Sharaf OZ, Orhan MF. An overview of fuel cell technology: Fundamentals and applications. Renewable and Sustainable Energy Reviews. 2014;**32**:810-853

[4] Fernandez Alvarez, G., 2011. Palladium Based Catalysts for Oxygen Reduction in Polymer Electrolyte Membrane Fuel Cells (Doctoral thesis, Newcastle University). [Accessed online, 28 February 2017]

[5] Lucia U. Overview on fuel cells. Renewable and Sustainable Energy Reviews. 2014;**30**:164-169

[6] Lai J, Ellis MW. Fuel cell power systems and applications. Proceedings of the IEEE. 2017;**105**:2166-2190

[7] Available from: https://cdn.shortpixel.ai/spai/q_lossy+ret_img/https://i2.wp.com/www.electroniclinic.com/wp-conte

[8] U.S. EERE U. Department of Energy's Office of Energy Efficiency and Renewable Energy. Geothermal Electricity Technology Evaluation Model (GETEM); 2016

[9] Antolini E. Palladium in fuel cell catalysis. Energy & Environmental Science. 2009;**2**(9):915-931

[10] Antolini E, Perez J. The renaissance of unsupported nanostructured catalysts for low-temperature fuel cells: From the size to the shape of metal nanostructures. Journal of Materials Science. 2011;**46**:4435-4457

[11] Lu Y, Tu JP, Gu CD, Xia XH, Wang XL, Mao SX. Growth of and methanol electro-oxidation by gold nanowires with high density stacking faults. Journal of Materials Chemistry. 2011;**21**(13):4843-4849

[12] Hogarth M, Ralph T. Catalysis for low temperature fuel cells. Platinum Metals Review. 2002;**46**:146-164

[13] Hamnett A. Mechanism and electrocatalysis in the direct methanol fuel cell. Catalysis Today. 1997;**38**:445-457

[14] Yajima T, Uchida H, Watanabe M. In-situ ATR-FTIR spectroscopic study of electro-oxidation of methanol and adsorbed CO at Pt− Ru alloy. The Journal of Physical Chemistry B. 2004;**108**(8):2654-2659

[15] Ambrosio EP, Francia C, Manzoli M, Penazzi N, Spinelli P. Platinum catalyst supported on mesoporous carbon for PEMFC. International Journal of Hydrogen Energy. 2008;**33**(12):3142-3145

[16] Lin Y, Cui X, Yen CH, Wai CM. PtRu/carbon nanotube nanocomposite synthesized in supercritical fluid: A novel electrocatalyst for direct methanol fuel cells. Langmuir. 2005;**21**(24):11474-11479

[17] Kim YI et al. Electrocatalytic properties of carbon nanofiber web-supported nanocrystalline Pt catalyst as applied to direct methanol fuel cell. International Journal of Electrochemical Science. 2009;**4**:1548-1559

[18] Maiyalagan T. Silicotungstic acid stabilized Pt–Ru nanoparticles supported

on carbon nanofibers electrodes for methanol oxidation. International Journal of Hydrogen Energy. 2009;**34**:2874

[19] Tiwari JN, Tiwari RN, Singh G, Kim KS. Recent progress in the development of anode and cathode catalysts for direct methanol fuel cells. Nano Energy. 2013;**2**(5):553-578

[20] Neto AO, Dias RR, Tusi MM, Linardi M, Spinacé EV. Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process. Journal of Power Sources. 2007;**166**(1):87-91

[21] Hassan HB. Electrodeposited Pt and Pt-Sn nanoparticles on Ti as anodes for direct methanol fuel cells. Journal of Fuel Chemistry and Technology. 2009;**37**(3):346-354

[22] Qi Z, Geng H, Wang X, Zhao C, Ji H, Zhang C, et al. Novel nanocrystalline PdNi alloy catalyst for methanol and ethanol electro-oxidation in alkaline media. Journal of Power Sources. 2011;**196**(14):5823-5828

[23] Lee SA, Park KW, Choi JH, Kwon BK, Sung YE. Nanoparticle synthesis and electrocatalytic activity of Pt alloys for direct methanol fuel cells. Journal of the Electrochemical Society. 2002;**149**(10):A1299

[24] Morante-Catacora TY, Ishikawa Y, Cabrera CR. Sequential electrodeposition of Mo at Pt and PtRu methanol oxidation catalyst particles on HOPG surfaces. Journal of Electroanalytical Chemistry. 2008;**621**(1):103-112

[25] Chen CS, Pan FM. Electrocatalytic activity of Pt nanoparticles deposited on porous TiO2 supports toward methanol oxidation. Applied Catalysis B: Environmental. 2009;**91**(3-4):663-669

[26] Xing L, Jia J, Wang Y, Zhang B, Dong S. Pt modified TiO2 nanotubes electrode: Preparation and electrocatalytic application for methanol oxidation. International journal of hydrogen energy. 2010;**35**(22):12169-12173

[27] Huang J, Yang H, Huang Q, Tang Y, Lu T, Akins DL. Methanol oxidation on carbon-supported Pt-Os bimetallic nanoparticle electrocatalysts. Journal of the Electrochemical Society. 2004;**151**(11):A1810

[28] Kang Y, Murray CB. Synthesis and electrocatalytic properties of cubic Mn−Pt nanocrystals (nanocubes). Journal of the American Chemical Society. 2010;**132**(22):7568-7569

[29] Kordesch K, Simader G. Fuel cells and their applications. 1996

[30] Léger J-M. Mechanistic aspects of methanol oxidation on platinum-based electrocatalysts. Journal of Applied Electrochemistry. 2001;**31**:767-771

[31] Lim C, Wang C. Development of high-power electrodes for a liquid-feed direct methanol fuel cell. Journal of Power Sources. 2003;**113**:145-150

[32] Papoutsis A, Léger JM, Lamy C. Study of the kinetics of adsorption and electro-oxidation of MeOH on Pt (100) in an acid medium by programmed potential voltammetry. Journal of Electroanalytical Chemistry. 1993;**359**(1-2):141-160

[33] Herrero E, Franaszczuk K, Wieckowski A. Electrochemistry of methanol at low index crystal planes of platinum: An integrated voltammetric and chronoamperometric study. The Journal of Physical Chemistry. 1994;**98**(19):5074-5083

[34] Biswas PC, Nodasaka Y, Enyo M. Electrocatalytic activities of

graphite-supported platinum electrodes for methanol electrooxidation. Journal of applied electrochemistry. 1996;**26**:30-35

[35] Burstein GT, Barnett CJ, Kucernak AR, Williams KR. Aspects of the anodic oxidation of methanol. Catalysis Today. 1997;**38**(4):425-437

[36] Lin WF, Wang JT, Savinell RF. On-line FTIR spectroscopic investigations of methanol oxidation in a direct methanol fuel cell. Journal of the Electrochemical Society. 1997;**144**(6):1917

[37] Zhu Y et al. Attenuated total reflection− Fourier transform infrared study of methanol oxidation on sputtered Pt film electrode. Langmuir. 2001;**17**(1):146-154

[38] Christensen PA, Hamnett A, Troughton GL. The role of morphology in the methanol electro-oxidation reaction. Journal of Electroanalytical Chemistry. 1993;**362**(1-2):207-218

[39] Pletcher D, Solis V. The effect of experimental parameters on the rate and mechanism of oxidation of methanol at a platinum anode in aqueous acid. Electrochimica Acta. 1982;**27**(6):775-782

[40] Yahikozawa K et al. Electrocatalytic properties of ultrafine platinum particles for oxidation of methanol and formic acid in aqueous solutions. Electrochimica Acta. 1991;**36**(5-6):973-978

[41] Kinoshita K. Particle size effects for oxygen reduction on highly dispersed platinum in acid electrolytes. Journal of the Electrochemical Society. 1990;**137**(3):845

[42] Takasu Y, Fujii Y, Matsuda Y. Size effects of small platinum particles on the electrocatalytic oxidation of methanol.

Bulletin of the Chemical Society of Japan. 1986;**59**(12):3973-3974

[43] Burke LD, Casey JK. Hydrous oxide formation on platinized platinum electrodes and its relevance to oxygen gas reduction. Berichte der Bunsengesellschaft für Physikalische Chemie. 1990;**94**(9):931-937

[44] Watanabe M, Saegusa S, Stonehart P. High platinum electrocatalyst utilizations for direct methanol oxidation. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry. 1989;**271**(1-2):213-220

[45] Frelink T, Visscher W, Van Veen JAR. Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol. Journal of Electroanalytical Chemistry. 1995;**382**(1-2):65-72

[46] Kennedy BJ, Hamnett A. Oxide formation and reactivity for methanol oxidation on platinised carbon anodes. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry. 1990;**283**(1-2):271-285

[47] Leung LWH, Michael J. Weaver. Influence of adsorbed carbon monoxide on electrocatalytic oxidation of simple organic molecules at platinum and palladium electrodes in acidic solution: A survey using real-time FTIR spectroscopy. Langmuir. 1990;**6**(2):323-333

[48] Marković NM, Gasteiger HA, Ross PN Jr, Jiang X, Villegas I, Weaver MJ. Electro-oxidation mechanisms of methanol and formic acid on Pt-Ru alloy surfaces. Electrochimica Acta. 1995;**40**:91-98

[49] Iwasita-Vielstich T. In: Gerischer H, Tobias CW, editors. Advances in Electrochemical Science and

Engineering. 1st ed. Weinheim: VCH; 1990. pp. 127-170

[50] Ma C, Chen Z, Zhao F. Synthesis of ultrafine mesoporous tungsten carbide by high-energy ball milling and its Electrocatalytic activity for methanol oxidation. Chinese Journal of Chemistry. 2011;**29**(4):611-616

[51] Zhong X, Zhang X, Sun X, Liu B, Kuang Y, Chen J. Pt and Pt-Ru nanoparticles dispersed on Ethylenediamine grafted carbon nanotubes as new Electrocatalysts: Preparation and Electrocatalytic properties for ethanol Electrooxidation. Chinese Journal of Chemistry. 2009;**27**(1):56-62

[52] Martínez-Huerta MV, Rojas S, De La Fuente JG, Terreros P, Pena MA, Fierro JL. Effect of Ni addition over PtRu/C based electrocatalysts for fuel cell applications. Applied Catalysis B: Environmental. 2006;**69**(1-2):75-84

[53] Pasupathi S, Tricoli V. Effect of third metal on the electrocatalytic activity of PtRu/Vulcan for methanol electro-oxidation. Journal of Solid State Electrochemistry. 2008;**12**:1093-1100

[54] Huang T, Liu J, Li R, Cai W, Yu A. A novel route for preparation of PtRuMe (me= Fe, Co, Ni) and their catalytic performance for methanol electrooxidation. Electrochemistry Communications. 2009;**11**(3):643-646

[55] Gurau B et al. Structural and electrochemical characterization of binary, ternary, and quaternary platinum alloy catalysts for methanol electro-oxidation. The Journal of Physical Chemistry B. 1998;**102**(49):9997-10003

[56] Choi WC, Kim JD, Woo SI. Quaternary Pt-based electrocatalyst for methanol oxidation by combinatorial

electrochemistry. Catalysis Today. 2002;**74**(3-4):235-240

[57] Arico AS et al. Characterization of direct methanol fuel cell components by electron microscopy and X-ray microchemical analysis. Materials Chemistry and Physics. 1997;**47**(2-3):257-262

[58] Aramata A, Masuda M. Platinum alloy electrodes bonded to solid polymer electrolyte for enhancement of methanol electro-oxidation and its reaction mechanism. Journal of the Electrochemical Society. 1991;**138**(7):1949

[59] Greenwood NN, Earnshaw A. Chemistry of the Elements. 2nd ed. Oxford: Butterworth-Heinemann; 1997

[60] Debe MK. Electrocatalyst approaches and challenges for automotive fuel cells. Nature. 2012;**486**(7401):43-51

[61] Steele BC, Heinzel A. Materials for fuel-cell technologies. Nature. 2001;**414**(6861):345-352

[62] Kim HJ, Ahn YD, Kim J, Kim KS, Jeong YU, Hong JW, et al. Surface elemental distribution effect of Pt-Pb hexagonal nanoplates for electrocatalytic methanol oxidation reaction. Chinese Journal of Catalysis. 2020;**41**(5):813-819

[63] Schultz MG, Diehl T, Brasseur GP, Zittel W. Air pollution and climate-forcing impacts of a global hydrogen economy. Science. 2003;**302**(5645):624-627

[64] Zhao X, Yin M, Ma L, Liang L, Liu C, Liao J, et al. Recent advances in catalysts for direct methanol fuel cells. Energy & Environmental Science. 2011;**4**(8):2736-2753

[65] Cruz JC, Baglio V, Siracusano S, Ornelas R, Arriaga LG, Antonucci V,

Aricò AS. Nanosized Pt/IrO2 electrocatalyst prepared by modified polyol method for application as dual function oxygen electrode in unitized regenerative fuel cells. International journal of hydrogen energy. 1 Apr 2012;**37**(7):5508-5517

[66] Baglio V, Di Blasi A, D'Urso C, Antonucci V, Aricò AS, Ornelas R, et al. Development of Pt and Pt–Fe catalysts supported on multiwalled carbon nanotubes for oxygen reduction in direct methanol fuel cells. Journal of the Electrochemical Society. 2008;**155**(8):B829

[67] Bezerra CW, Zhang L, Liu H, Lee K, Marques AL, Marques EP, et al. A review of heat-treatment effects on activity and stability of PEM fuel cell catalysts for oxygen reduction reaction. Journal of Power Sources. 2007;**173**(2):891-908

[68] Valisi AN, Maiyalagan T, Khotseng L, Linkov V, Pasupathi S. Effects of heat treatment on the catalytic activity and methanol tolerance of carbon-supported platinum alloys. Electrocatalysis. 2012;**3**(2):108-118

[69] Li X, Liu J, Huang Q, Vogel W, Akins DL, Yang H. Effect of heat treatment on stability of gold particle modified carbon supported Pt–Ru anode catalysts for a direct methanol fuel cell. Electrochimica Acta. 2010;**56**(1):278-284

[70] Chaisubanan N, Maniwan W, Hunsom M. Effect of heat-treatment on the performance of PtM/C (M= Cr, Pd, Co) catalysts towards the oxygen reduction reaction in PEM fuel cell. Energy. 2017;**127**:454-461

[71] Kamarudin SK, Achmad F, Daud WRW. Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. International

Journal of Hydrogen Energy. 2009;**34**:6902-6916

[72] Gerwith AA, Thorum MS. Electroreduction of dioxygen for fuel-cell applications: Materials and challenges. Inorganic Chemistry. 2010;**49**:355

[73] Janssen MMP, Moolhuysen J. Platinum—tin catalysts for methanol fuel cells prepared by a novel immersion technique, by electrocodeposition and by alloying. Electrochimica Acta. 1976;**21**:861

[74] Wang H, Li H, Yan X. PEM Fuel Cell Failure Mode Analysis. 2011. p. 53

[75] Ang S, Walsh AD. Palladium–vanadium alloy electrocatalysts for oxygen reduction: Effect of heat treatment on electrocatalytic activity and stability. Applied Catalysis B: Environmental. 2010;**98**:49-56

[76] Jeng KT, Chien CC, Hsu NY, Yern SC, Chiou SD, Lin SH, et al. Performance of direct methanol fuel cell using carbon nanotube-supported Pt–Ru anode catalyst with controlled composition. Journal of Power Sources. 2006;**160**:97

[77] Khotseng L, Bangisa A, Modibedi RM, Linkov V. Electrochemical evaluation of Pt-based binary catalysts on various supports for the direct methanol fuel cell. Electrocatalysis. 2016;**7**:1-12

[78] Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP. A review of anode catalysis in the direct methanol fuel cell. Journal of Power Sources. 2006;**155**(2):95-110

[79] Kumar SS, Hidyatai N, Herrero JS, Irusta S, Scott K. Efficient tuning of the Pt nano-particle mono-dispersion on Vulcan XC-72R by selective pre-treatment and electrochemical

evaluation of hydrogen oxidation and oxygen reduction reactions. International Journal of Hydrogen Energy. 2011;**36**(9):5453-5465

[80] Garsany Y, Baturina OA, Swider-Lyons KE, Kocha SS. Experimental methods for quantifying the activity of platinum electrocatalysts for the oxygen reduction reaction. Analytical Chemistry. 2010;**82**:6321-6328

[81] Vielstich W, Gasteiger HA, Lamm A. Handbook of Fuel Cells Fundamentals, Technology and Applications. Vol. 2. New York, NY: Wiley; 2003. p. 316. ISBN 0 471 49926 9; TRN: GB0400273

[82] Uchida M, Aoyama Y, Tanabe M, Yanagihara N, Eda N, Ohta A. Influences of both carbon supports and heat-treatment of supported catalyst on electrochemical oxidation of methanol. Journal of the Electrochemical Society. 1995;**142**(8):2572