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Chapter

Investigation of Synthesis Methods for Improved Platinum-Ruthenium Nanoparticles Supported on Multi-Walled Carbon Nanotube Electrocatalysts for Direct Methanol Fuel Cells

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Abstract

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

Keywords: methanol oxidation, catalysts, multi-walled carbon nanotubes, electrocatalytic activity

1. Introduction

Catalyst synthesis methods have an influence on mean particle size, particle size distribution, the bulk and surface of catalysts' composition, the oxidation state of catalysts, the extent of catalyst alloying, the distribution of catalyst crystal surfaces, and catalyst morphology [1, 2], and hence on the catalytic activity of the metal

catalysts [3]. The standard by which high-performance catalysts are evaluated includes a uniform composition in the entire nanoparticles, a complete alloying degree, a narrow nanoscale size distribution, and high dispersion on carbon support [4]. Various methods for the synthesis of fuel cell catalysts have been reported in the literature, including micro-emulsion, sputtering, and co-precipitation methods. In this study, we report on the synthesis of catalysts using the impregnation, polyol, modified polyol, and microwave-assisted modified polyol methods.

1.1 Impregnation method

The impregnation approach is frequently utilized for the manufacture of Pt-based catalysts. It is a straightforward chemical preparation process for catalyst synthesis that can create tiny particles in the 3–7 nm range with regulated loading [5, 6]. The impregnation method for the synthesis of platinum-ruthenium (PtRu) includes an impregnation step in which Pt and Ru precursor salts are mixed with the support material, which is typically high-surface-area porous or nanostructured carbon and penetrates into pores. The catalyst support aids in the penetration and wetting of the precursor and the carbon support confines the particle size growth during the reduction step. The chemical reduction can be carried out in the liquid phase with a reductive agent such as $\text{Na}_2\text{S}_2\text{O}_3$, NaBH_4 , $\text{Na}_4\text{S}_2\text{O}_5$, N_2H_4 or formic acid, or in the gas phase with a reductive agent such as a flowing hydrogen stream at elevated temperatures. The difficulty in adjusting nanoparticle size and distribution is a key limitation of the impregnation process [5, 6]. It has been noted that impregnated catalysts have a tendency to generate inhomogeneous agglomerations of active species at the support boundary, resulting in large-sized particles [1].

Other difficulties include the use of chloride precursors, which could result in chloride poisoning and decreased catalytic activity and stability of the chloride-salt-produced catalyst. Metal nitrate/nitrite salts such as $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ and $\text{RuNO}(\text{NO}_3)_x$ [7], carbonyl complexes such as $\text{Ru}_3(\text{CO})_{12}$ [8], and metal sulfite salts such as $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ and $\text{Na}_6\text{Ru}(\text{SO}_3)_4$ [9] as metal precursors for Pt and Ru, respectively, have been investigated for impregnation methods that could use chloride-free precursors. When compared to the traditional Cl-containing route, these chloride-free pathways provide improved dispersion and catalytic activity. In this chapter, we report on an impregnation method where NaBH_4 was used as the reducing agent and ethylene glycol (EG) as the solvent.

1.2 Polyol reduction method

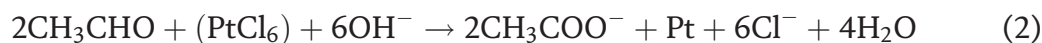
The polyol method includes the following common steps: (1) preparation of Pt-containing colloids; (2) deposition of the colloids onto the support, and (3) chemical reduction of the mixture. The synthesis occurs in an organic or aqueous medium where the metal precursor is reduced chemically in the presence of a protective agent (i.e., NR41, PPh_3 , PVP, SB12, or PVA). Other colloid methods using several reducing agents, organic stabilizers, or shell-removing approaches have also been developed in recent years. The catalyst is supported with catalyst support to enhance the surface area and the dispersion of the catalyst. To achieve a limited size distribution, the colloidal metal nanoparticles are stabilized by steric hindrance or electrostatic charges. Coating the metal core with organic chain molecules can offer steric stability [10, 11]. The aggregation of charged colloids or adsorbed ions is limited by the electrostatic repulsion of similar charges. The use of protective agents, which may influence the catalytic activity of the nanoparticles, poses a problem for the polyol process, but it may be removed by washing in a suitable solvent or breakdown at temperatures in an inert atmosphere. There are also other

challenges facing the polyol method, such as that it is time-consuming, complex, and expensive, which causes difficulty in terms of scaling up. The colloidal method prepares catalysts with nanoparticle size and narrow size distribution.

The polyol method that was employed in this study has been extensively explored as a preparation method for Pt [5, 12].

1.3 Modified polyol reduction method

Fievet et al. [13] pioneered the use of EG as both a solvent and a reducing agent. They found that EG may support colloidal metal particles in solution, resulting in a well-distributed solution. EG has a relatively high viscosity, and therefore it prevents Pt from being delivered to reaction sites too quickly, resulting in reduced Pt particle sizes [14]. This method is called the modified polyol method [15]. The modified polyol method is able to effectively synthesize very small and well-dispersed metal nanoparticles [2]. However, the synthesis parameters such as the water: EG ratio, the concentration of EG, and the pH of the solution have a great effect on the characteristics of the results [2]. Bimetallic catalysts, metal oxides, and metal sulfides with narrow particle size distributions, controlled compositions, and alloy structures have also been effectively prepared using the modified polyol technique [16]. The modified polyol approach, which uses EG as a reducing agent and solvent, was also used to make catalysts in this study. EG was utilized as both a reducing agent and a solvent for the Pt and Ru precursors in this method. The solution of EG, Pt, and Ru precursor salts was heated to 120–170°C during the reduction phase. EG is decomposed in this step, resulting in the reducing species (CH₃CHO-acetaldehyde, Eq. (1)) [17].



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

1.4 Microwave-assisted modified polyol methods

The microwave synthetic approach was one of the methods employed in this study. A modified polyol method has been reported for this technique, with the deposition and reduction steps taking place in a microwave reactor. Microwave synthetic methodology has been utilized to manufacture catalysts because of its fast, uniform, homogeneous, and instant heating environment, which resulted in rapid reduction and facilitated metal particle nucleation [8, 18]. Microwave heating is a promising technology, with its applications rapidly growing due to its advantages over conventional heating, such as rapid volumetric heating, which increased reaction rates and shortened reaction time; however, to induce crystallization, a post-synthesis heat treatment was required [3]. Under such conditions, a microwave-assisted synthesis method is an appropriate option, with the added benefits of narrow size distribution and high purity [4]. At high pH conditions for depositions, promising results were reported with an average Pt size of 2.7 nm. However, because the reaction takes place in a closed system, the pH cannot be

controlled throughout the duration of the reaction, hence, the entire scope of the reaction under these conditions is unknown [19].

2. Results and discussion

2.1 Physical characterization of the prepared electrocatalysts

X-ray diffraction (XRD) and the high-resolution transmission electron microscope (HRTEM) were used to learn more about the catalyst structure. The XRD patterns were performed with the Bruker AXS D8 advance equipment with Cu-K radiation and a wavelength of 1.5406 nm. With a scanning step of 0.035°, the Bragg angle range was $2\theta = 10\text{--}90^\circ$. The instrumental contribution to peak profile characteristics was determined using a standard $\alpha\text{-Al}_2\text{O}_3$ sample. A JEOL 2010 TEM system operating at 200 kV was used to obtain the HRTEM micrographs. The HRTEM samples were made by dispersing the carbon-supported electrocatalysts in ethanol and then casting a drop of the suspension onto a Cu-grid covered in carbon film for analysis. For each electrocatalyst, the particle size determined by HRTEM was obtained using Image J software over multiple areas.

2.2 XRD analysis

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

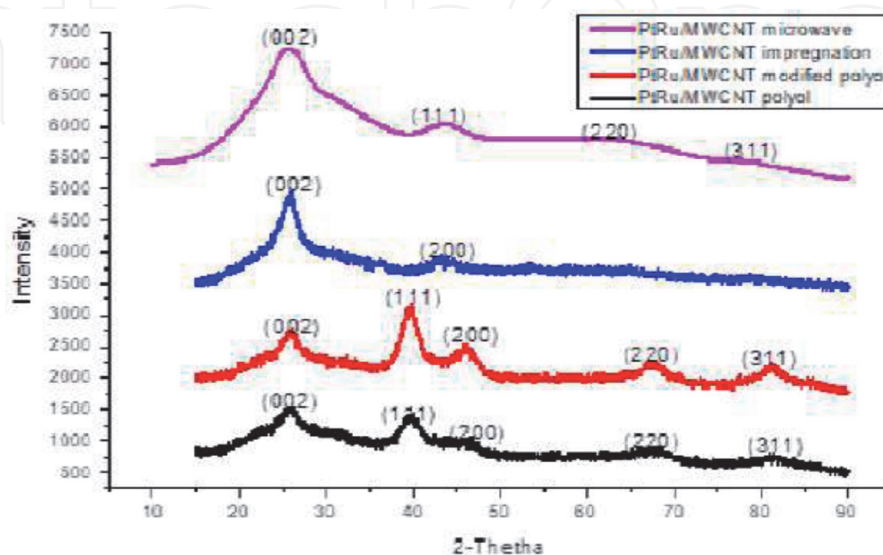


Figure 1. XRD spectra of PtRu electrocatalysts supported on multi-walled carbon nanotubes (MWCNTs) prepared through the impregnation, polyol, modified polyol, and microwave-assisted modified polyol methods.

(311), respectively. Similar results were also reported by Kim et al. [20] and Wu et al. [21].

The crystalline size of the metal particles is calculated using Debye-Scherrer's equation, $K\alpha/\beta\cos\theta$, where K, Scherrer constant = 0.9, α , X-ray wavelength = 0.154 nm, and $\beta(2\theta)$, the width of the diffraction peak (rad). From **Table 1** the average particle size can be seen, with PtRu/MWCNT nanoparticles prepared through microwave-assisted modified polyol having the smallest crystalline size of 1.95 nm, followed by PtRu/MWCNT nanoparticles prepared through the modified polyol method with a crystalline size of 4.33 nm.

Catalyst nanoparticles are the dark dots as shown in the HRTEM micrographs in **Figure 2**. PtRu/MWCNT nanoparticles are well distributed with little agglomeration. PtRu/MWCNT electrocatalysts prepared through the microwave-assisted modified polyol method has the least agglomeration, followed by PtRu/MWCNT modified polyol when compared with other electrocatalysts evident from their higher electroactive catalyst surface areas of $4.15 \times 10^2 \text{ m}^2/\text{g}$ and $3.2 \times 10^2 \text{ m}^2/\text{g}$, respectively an advantage for enhanced electrocatalytic activities. Both of these catalysts gave the smallest particle sizes of 1.87 and 4.14 nm, respectively. The other electrocatalysts PtRu on MWCNT support particle sizes were between 5.77 and 6.90 nm. The particle sizes of the electrocatalysts obtained were comparable with the average particle sizes following the order PtRu/MWCNT impregnation > PtRu/MWCNT polyol > PtRu/MWCNT modified polyol > PtRu/MWCNT microwave-assisted modified polyol.

In **Figure 2** the histograms reveal the mean particle sizes and their nanoparticle size distributions for all PtRu/MWCNT electrocatalysts prepared through all four synthesis methods; however, the two electrocatalysts prepared through the impregnation method and polyol method exhibited better distribution of nanoparticles as compared to other electrocatalysts. The particle size was determined using Image J software estimated from 50 particles selected randomly from HRTEM micrographs of the PtRu/MWCNT nanoparticles. The mean particle sizes of PtRu/MWCNT impregnation, PtRu/MWCNT polyol, PtRu/MWCNT modified polyol, and PtRu/MWCNT microwave-assisted modified polyol were 6.90, 6.51, 4.14, and 1.87 nm, respectively.

2.3 Electrochemical characterization of the electrocatalysts

Electrochemical measurements were carried out at ambient temperatures using a three-electrode configuration, which includes a working electrode, a counter electrode, and a reference electrode. An Ag/AgCl electrode as a reference electrode and a Pt foil of a large area as a counter electrode were used. The working electrode was a glassy carbon disc (5 mm in diameter with a geometric area of 0.196 cm^2) covered with a thin layer of catalyst of fine film. Before the experiment, the electrode substrate was pre-treated by polishing it with a $0.05 \mu\text{m Al}_2\text{O}_3$ particle suspension on a moistened microcloth. All the electrochemical experiments were carried out, namely electrochemical impedance spectroscopy (EIS),

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

Table 1.
Properties of the PtRu electrocatalysts.

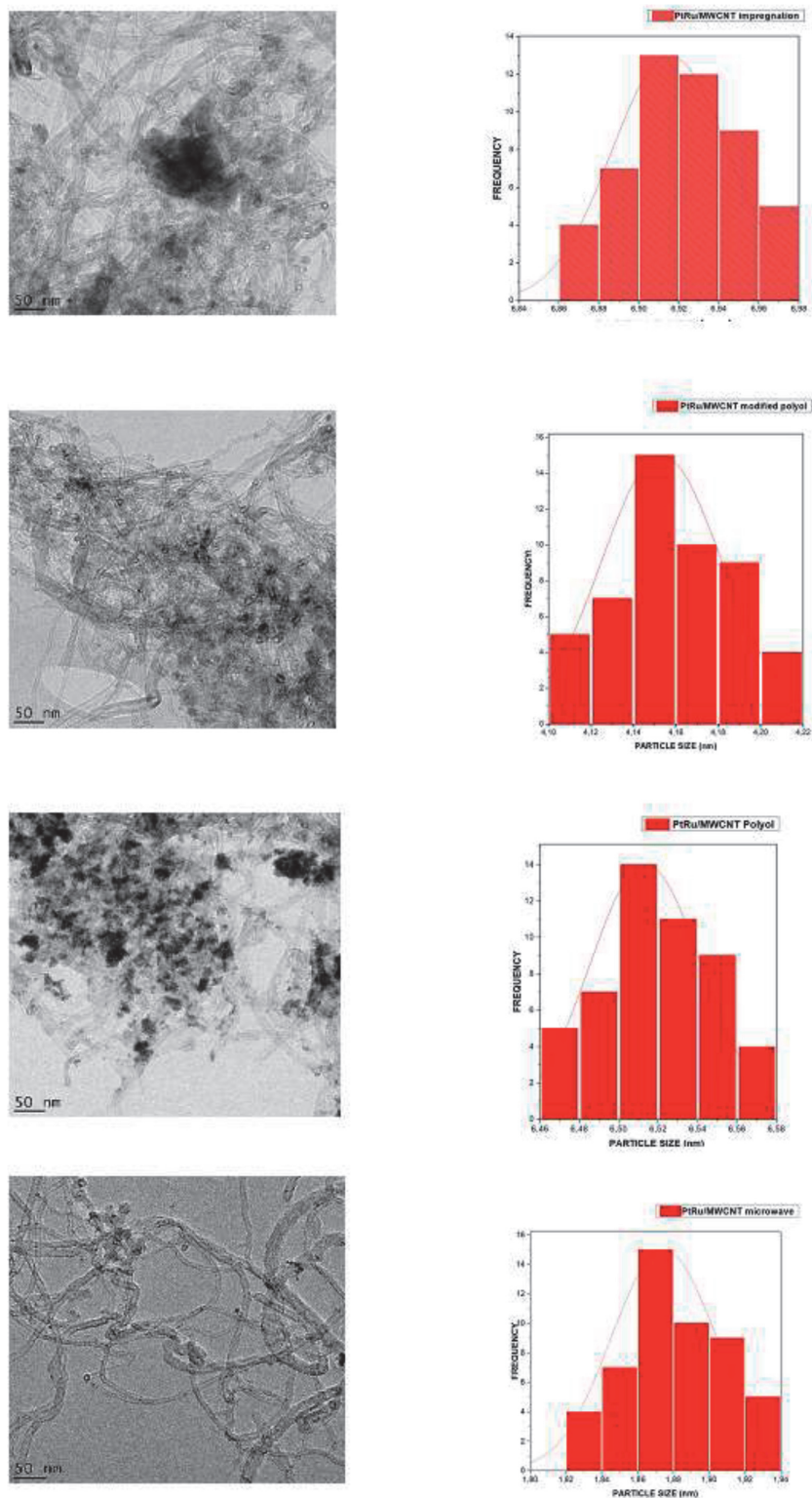


Figure 2. HRTEM images with their respective histograms for PtRu/MWCNT prepared through the impregnation, polyol, modified polyol, and microwave-assisted modified polyol methods.

chronoamperometry (CA), and cyclic voltammetry (CV), and performed on an autolab electrochemical workstation (PGSTAT128N, Eco Chemie, the Netherlands). CA tests were carried out for the electrocatalytic stability of the PtRu/MWCNT catalysts for the methanol electro-oxidation. The CA was carried out for 30 minutes. CV evaluations were carried out at 30 mV/s covering a potential window from -0.2 to 1.2 V vs. Ag/AgCl. Perchloric acid was used as the electrolyte. Inert nitrogen gas was used to deaerate the solutions. To obtain a homogeneous catalyst layer, a stock solution was first prepared by mixing 20 ml of isopropanol, 79.6 ml of ultra-pure

water, and 0.4 ml of 5wt% Nafion solution in a 100-ml volumetric flask. Thereafter, 10 mg of the catalyst powder was measured into a 10-ml vial and 5 ml of stock solution was added, mixed thoroughly, and sonicated for 60 minutes in an ultrasonicator. A measured volume of this mixture was dropped on top of the glassy carbon disc and then dried to form the desired catalyst layer.

Electrochemical activities of the prepared catalysts in a 0.5 M HClO₄ solution were firstly examined by CV. From the CV of the prepared electrocatalysts, the adsorption peaks for the different catalysts were observed. The peak area of the adsorption peak of the electrocatalysts in the CV was used to determine the electroactive surface area of the catalysts using the equation 2 [22]:

$$ECSA = \frac{Q}{210 \mu C/cm^2.m.Ag} \quad (3)$$

where Q is the charge from the adsorption peak in Coulomb taking within the negative potential region of -0.2 to 0.08 V in the forward scan, as shown in **Figure 3**, m is the working electrode Pt loading in $mg\ cm^{-2}$, Ag is the geometric surface area of the electrode (5 mm in diameter, $Ag = 0.196\ cm^2$) and $210\ \mu C\ cm^{-2}$ is the value for the charge of full coverage for a clean polycrystalline Pt monolayer [23].

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

2.4 Methanol oxidation

The electrocatalytic activity of the PtRu/MWCNT series catalysts towards the methanol oxidation was investigated using the CV technique in 0.5 M HClO₄ with 2 M methanol at a scan rate of $30\ mVs^{-1}$, as shown in **Figure 4**.

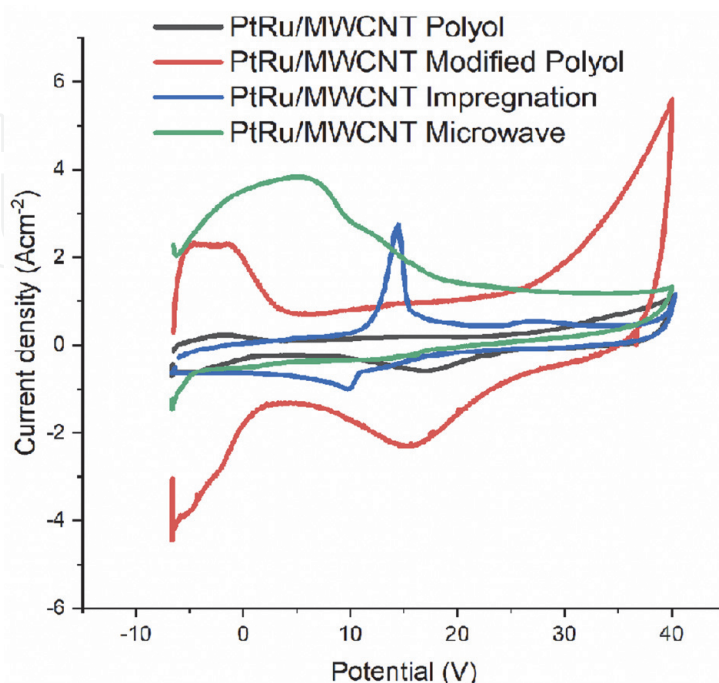


Figure 3. Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N₂-saturated 0.5 M perchloric acid HClO₄ at a scan rate of $30\ mV.s^{-1}$.

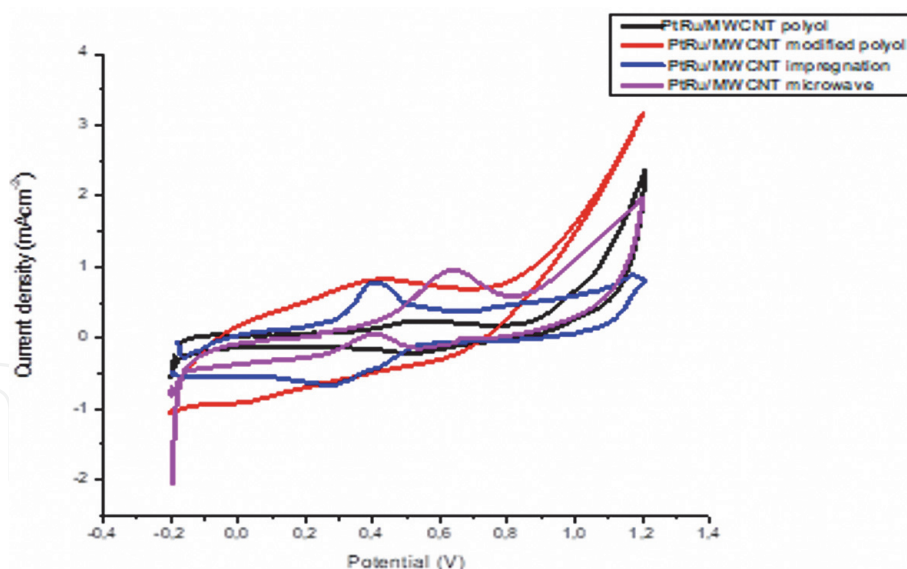


Figure 4. Cyclic voltammograms of PtRu/MWCNT electrocatalysts in N_2 -saturated 0.5 M perchloric acid $HClO_4$ and 2 M methanol at a scan rate of $30 \text{ mV}\cdot\text{s}^{-1}$.

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

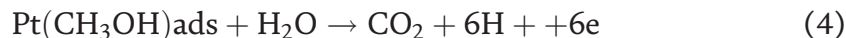
[a] Onset potential, [b] forward anodic peak potential at 30 mVs^{-1} , [c] forward anodic peak current density at 30 mVs^{-1} .

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

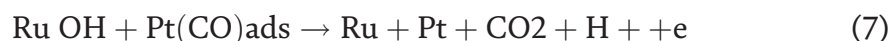
The electrocatalytic activity towards methanol oxidation is summarized in **Table 2**. By comparing the characteristics of the CVs, the change in catalyst preparation methods leading to varying compositions of Pt and Ru in the metal alloys was found to substantially enhance the catalytic activity for methanol electro-oxidation. First, the onset potentials (a measure of catalytic activity) of methanol oxidation for the PtRu/MWCNT prepared through the microwave-assisted modified polyol method and PtRu/MWCNT showed relatively lower values than that of PtRu/MWCNT electrocatalysts prepared through the impregnation, polyol and modified polyol methods. The positions of the onset potentials follow the order of PtRu/MWCNT microwave-assisted modified polyol < PtRu/MWCNT modified polyol < PtRu/MWCNT polyol < PtRu/MWCNT impregnation. Second, the forward peak current densities (measure of the maximum catalyst performance) of the PtRu/MWCNT catalysts took the order PtRu/MWCNT microwave-assisted modified polyol > PtRu/MWCNT impregnation > PtRu/MWCNT modified polyol > PtRu/MWCNT polyol. Therefore, PtRu/MWCNT prepared through the microwave-assisted modified polyol method exhibited the most prominent electrochemical performance in terms of the highest forward peak current density and the lowest onset potential, followed by PtRu/MWCNT prepared through the modified polyol method.

It was found that PtRu/MWCNT produced through the microwave-assisted modified polyol method of Pt: Ru ratio close to 1:1 outperformed all other PtRu/MWCNT electrocatalysts produced through other synthesis methods in methanol electro-oxidation reaction evident from the current density of 0.190 mA/cm².

Electro-oxidation of methanol to form CO₂ can be via dual path mechanisms consisting of non-CO and adsorbed CO reactive intermediates [24]:



The non-CO reaction pathway is preferred for methanol oxidation for which it does not involve CO, a poison for Pt metal. The adsorbed CO reaction pathway often presents, however, in which the intermediates via (CO)_{ads} are mostly in the form of linearly bonded CO, that is, Pt = C = O [25]. Interaction of this complex on the catalyst surface leads to CO poisoning. The presence of Ru in the bimetallic catalyst assists in the oxidation of CO through chemisorbed -OH on the Ru sites [26]:



In this way, the poisoned Pt is regenerated and can again participate in the oxidation of methanol. Due to the single species of CO and OH on Pt and Ru, respectively, the best results can be obtained when the Pt to Ru atomic ratio is 1:1 [27] (Figure 5).

The EIS technique was used to investigate the catalytic reaction kinetics for the methanol oxidation on the anodic PtRu/MWCNT electrocatalysts surfaces. The charge transfer resistance (R_{ct}) values using equivalent circuit fitting were 5.985, 8.926, 4.061, and 6.184 kΩ for PtRu/MWCNT modified polyol, PtRu/MWCNT polyol, PtRu/MWCNT impregnation, and PtRu/MWCNT microwave-assisted modified polyol, respectively, indicating that PtRu/MWCNT prepared through the

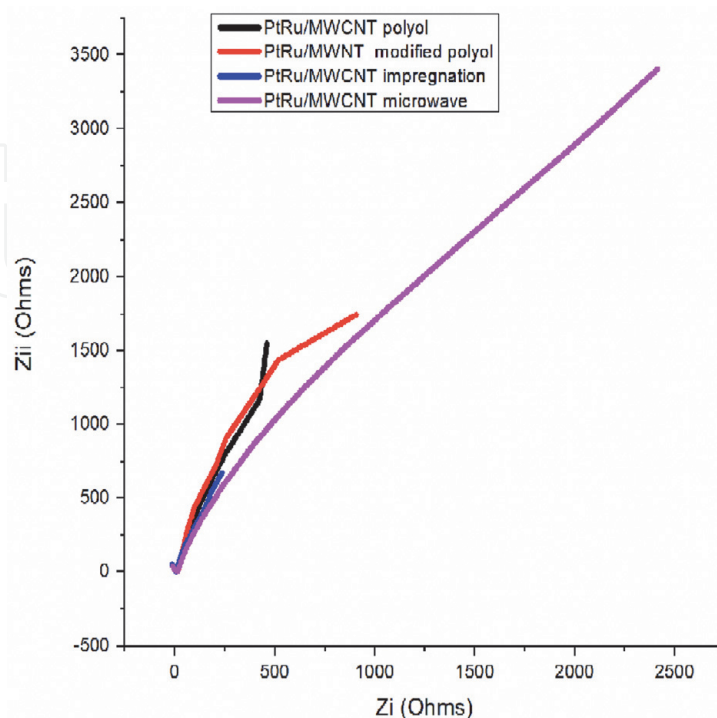


Figure 5. Electrochemical impedance curves of methanol oxidation on PtRu/MWCNT electrocatalysts prepared through different synthesis methods in N₂-saturated 0.5 M HClO₄ and 0.2 M methanol.

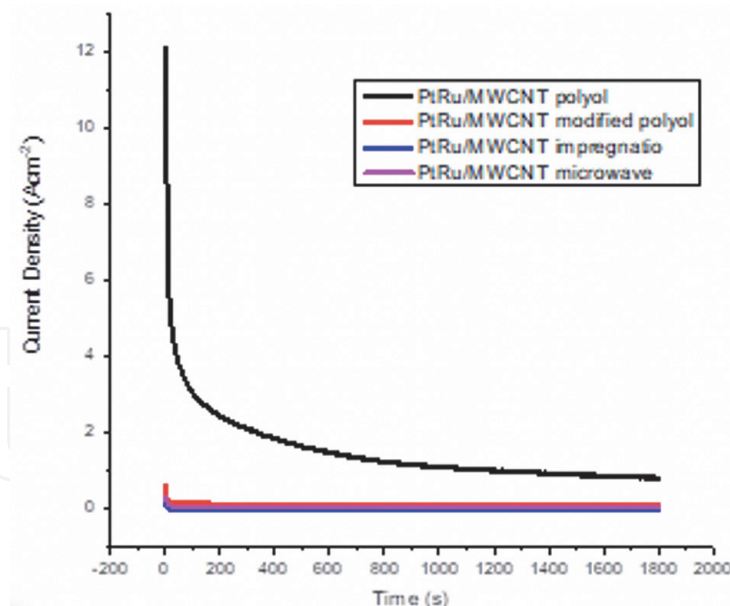


Figure 6. Chronoamperometry curves of methanol oxidation on PtRu/MWCNT electrocatalysts in 0.5 M HClO₄ and 2.0 M CH₃OH.

impregnation method exhibited the best kinetics towards the methanol electro-oxidation with the least resistance to flow of electric current. PtRu/MWCNT prepared through the modified polyol method also showed promising kinetics with an Rct value of 5.985 kΩ.

The stability of the electrocatalysts is extremely important for their real applications in direct methanol fuel cells. **Figure 6** shows the CA of PtRu electrocatalysts on MWCNT support in N₂-saturated 0.5 M HClO₄ with 2.0 M methanol. This was to test the stability of the different catalysts after 1800 seconds. As observed at the start of the CA curve, the current density decreases sharply with time (I proportional to $t^{-1/2}$). The decreasing rate with time may characterize the inhibition of the electrodes by the methanol oxidation reaction products. When comparing the prepared catalysts, PtRu/MWCNT catalyst prepared through the polyol method performed better, followed by PtRu/MWCNT modified polyol. PtRu/MWCNT prepared by microwaving also showed better stability with higher current density than PtRu/MWCNT prepared through the impregnation method.

3. Conclusion

In this study, PtRu, supported by MWCNT, was successfully fabricated using the impregnation, polyol, modified polyol, and microwave-assisted modified polyol catalyst preparation methods. The synthesized electrocatalysts had crystalline sizes of 1.95–7.11 nm and average particle sizes of 1.87–6.90 nm, determined using XRD and HRTEM, respectively. The PtRu alloy phase is pronounced for the prepared electrocatalysts according to XRD analysis. It is found that the PtRu/MWCNT electrocatalyst produced through the microwave-assisted modified polyol method and PtRu/MWCNT modified polyol showed enhanced electrocatalytic activity towards methanol oxidation compared to other PtRu electrocatalysts on MWCNT support. Furthermore, the microwave-assisted prepared PtRu/MWCNT electrocatalyst had the largest current density for methanol oxidation compared to other electrocatalysts. This can be attributed to it having the smallest particle size and being the most active toward anode oxidation reaction. From the EIS, it was

concluded that the PtRu/MWCNT electrocatalysts produced through the impregnation method exhibited a faster electrochemical reaction kinetics than both PtRu/MWCNT electrocatalysts produced through the polyol and modified polyol methods. Microwave-assisted modified polyol method PtRu electrocatalysts had the highest ECSA values compared to all other PtRu catalysts on MWCNT support, followed by PtRu/MWCNT produced by the modified polyol method. This was as a result of their smaller crystalline particle sizes of 1.95 and 4.33 nm, respectively. Polyol method synthesized PtRu/MWCNT was found to be the most stable electrocatalyst, followed by PtRu/MWCNT produced through the modified polyol method, as revealed by the chronoamperometry tests.

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

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References

- [1] Zhenlü W, Qingsheng L, Jianfeng Y, Tonghao W, Guojia W. Surface structure and catalytic behavior of silica-supported coppercatalysts prepared by impregnation and sol-gel methods. *Applied Catalysis*. 2003;**239**: 87-94. DOI: 10.1016/S0926-860X(02)00421-0
- [2] Lim B, Kim JW, Hwang SJ, Yoo SJ, Cho EA, Lim T-H, et al. Fabrication and characterization of high activity Pt/C electrocatalysts for oxygen reduction. *Bulletin of the Korean Chemical Society*. 2010;**31**(6):1577. DOI: 10.5012/bkcs.2010.31.6.1577
- [3] Krishnakumara T, Nicola P, Prasanna K, Perumala K, Jayaprakash R. Microwave-assisted synthesis and characterization of tin oxide nanoparticles. *Materials Letters*. 2008; **62**:3437-3440. DOI: 10.1016/j.matlet.2008.02.062
- [4] Aarti SB, Denthaje KB, Cheuk-Wai T, Mysore SS. Microwave-assisted synthesis and magnetic studies of cobalt oxide nanoparticles. *Materials Chemistry and Physics*. 2011;**125**: 347-350. DOI: 10.1016/j.matchemphys.2010.11.003
- [5] Dutrow BL, Clark CM. X-ray Powder Diffraction (XRD): Geochemical Instrumentation and Analysis. Available from: https://serc.carleton.edu/research_education/geochemsheet/techniques/XRD.html
- [6] Kumar SMS, Hidyatai N, Herero JS, Irusta S, Scott K. Efficient tuning of the Pt nano-particles 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**: 5453-5465. DOI: 10.1016/j.ijhydene.2011.01.124
- [7] Takasu Y, Fujiwara T, Murakami Y. Effect of structure of carbon-supported PTRU electrocatalysts on the electrochemical oxidation of methanol. *Journal of the Electrochemical Society*. 2000;**147**:4421-4427. DOI: 10.1149/1.1394080
- [8] Dickinson AJ, Carrette LPL, Collins JA, Friedrich KA, Stimming U. Preparation of a Pt-Ru/C catalyst from carbonyl complexes for fuel cell applications. *Electrochimica Acta*. 2002;**47**:3733. DOI: 10.1016/S0013-4686(02)00343-2
- [9] Friedrich KA, Geyzers KP, Dickinson AJ, Stimmin U. Fundamental aspects in electrocatalysis: From the reactivity of single-crystals to fuel cell electrocatalysts. *Journal of Electroanalytical Chemistry*. 2002;**261**: 524-525. DOI: 10.1016/S0022-0728(02)00731-3
- [10] Bonnemann H, Richards RM. Nanoscopic metal particles-synthetic methods and potential applications. *European Journal of Inorganic Chemistry*. 2001;**10**:2455
- [11] Roucoux A, Schulz J, Patin H. Reduced transition metal colloids: A novel family of reusable catalysts? *Chemical Reviews*. 2002;**102**:3757. DOI: 10.1021/cr010350j
- [12] Tang X, Li Y, Xu Y, Xin Q, Shen W. Structural features and catalytic properties of Pt/CeO₂ catalyst prepared by the modified reduction-deposition techniques. *Catalysis Letters*. 2004;**97**: 163-169
- [13] Fievet F, Lagier JP, Figlarz M. Preparing monodisperse metal powders in micrometer and submicrometer sizes by the polyol process. *MRS Bulletin*. 1989;**14**:29
- [14] Santiago EI, Varanda LC, Villulas HM. Carbon-supported Pt-Co

- catalysts prepared by a modified polyol process as cathodes for PEM fuel cells. *The Journal of Physical Chemistry*. 2007;**111**:3146. DOI: 10.1021/jp0670081
- [15] Available from: <http://www.strem.com/uploads/>
- [16] He B, Chen Y, Liu H, Liu Y. Synthesis of solvent-stabilized colloidal nanoparticles of platinum, rhodium, and ruthenium by microwave-polyol process. *Journal of Nanoscience and Nanotechnology*. 2005;**5**:266
- [17] Chiang YC, Lin WH, Chang YC. The influence of treatment duration on multi-walled carbon nanotubes functionalized by H₂SO₄/HNO₃ oxidation. *Applied Surface Science*. 2011;**257**:2401-2410
- [18] Machida K, Fukuoka A, Ichikawa M, Enyio M. Preparation of platinum cluster-derived electrodes from metal carbonyl complexes and their electrocatalytic properties for anodic oxidation of methanol. *Journal of the Electrochemical Society*. 1958;**1991**:138
- [19] Knupp S, Li W, Paschos O, Murray T, Snyder J, Haldar P. The effect of experimental parameters on the synthesis of carbon nanotube/nanofiber supported platinum by polyol processing techniques. *Carbon*. 2008;**46**:1276
- [20] Kim Y, Kim HW, Lee S, Han J, Lee D, Kim JR, et al. The role of ruthenium on carbon-supported PtRu catalysts for electrocatalytic glycerol oxidation under acidic conditions. *ChemCatChem*. 2017;**9**(9):1683-1690. DOI: 10.1002/cctc.201601325
- [21] Wu B, Zhu J, Li X, Wang X, Chu J, Xiong S. PtRu nanoparticles supported on p-phenylenediamine-functionalized multiwalled carbon nanotubes: Enhanced activity and stability for methanol oxidation. *Ionics*. 2019;**25**:181-189. DOI: 10.1007/s11581-018-2590-7
- [22] 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
- [23] Vielstich W, Gasteiger HA, Lamm A, editors. *Handbook of Fuel Cells—Fundamentals, Technology and Applications*. Vol. 2. New York, NY: Wiley; 2003. p. 316. ISBN 0 471 49926 9; TRN: GB0400273
- [24] Herrero E, Chrzanowski W, Wieckowski A. Dual path mechanism in methanol electrooxidation on a platinum electrode. *The Journal of Physical Chemistry*. 1995;**99**:10423. DOI: 10.1021/j100025a054
- [25] Manohara R, Goodenough JB. Methanol oxidation in acid on ordered NiTi. *Journal of Materials Chemistry*. 1992;**2**:875. DOI: 10.1039/JM9920200875
- [26] Meriaudeau P, Ellestad OH, Dufaux M, Naccache C. Metal-support interaction. Catalytic properties of TiO₂-supported platinum, iridium, and rhodium. *Journal of Catalysis*. 1982;**75**: 243. DOI: 10.1016/0021-9517(82)90206-8
- [27] Arico AS, Srinivasan S, Antonucci V. DMFCs: From fundamental aspects to technology development. *Fuel Cells*. 2001;**1**:133. DOI: 10.1002/1615-6854(200107)1:2<133::AID-FUCE133>3.0.CO;2-5