African Journal of Engineering and Environment Research Vol.6(2) 2024
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DOI: https://doi.org/10.37703
The link to this publication is https://ajoeer.org.ng/otn/ajoeer/2024/qtr-3/01.pdf

Pt-Co/rGO Electro-Catalysts for Methanol Electro-Oxidation Reaction in Direct Methanol Fuel Cell

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ABSTRACT

Pt-Co/rGO electro-catalysts were synthesized using reduced graphene oxide (rGO) as a support material. The rGO was produced from graphite powder by preparing graphene oxide (GO) via improved Hummer's method. A graphene oxide slurry was formed and mixed with 200 ml of distilled water and irradiated for 15 minutes at 50 °C by an ultrasonic technique. It was then filtered and dried at 80 °C for 40 hours to produce reduced graphene oxide (rGO). The methanol electro-oxidation catalysts were prepared using hexachloroplatinic (IV) hexahydrate and cobalt (II) nitrate hexahydrate as precursors for the metal active species. The developed Pt-Co/rGO electro-catalysts were characterized using XRD, SEM, EDX and BET. The Pt-Co/rGO electro-catalysts showed potential to be used for the methanol electro-oxidation reaction in direct methanol fuel cell.

Keywords: Reduced Graphene Oxide, Catalyst Support, Methanol Electro-catalysts and Direct Methanol Fuel Cell

DOI: https://doi.org/10.37703
https://ajoeer.org.ng/otn/ajoeer/2024/qtr-3/01.pdf

INTRODUCTION

Despite the advantages of the direct methanol fuel cell (DMFC), low anode electro-oxidation kinetics and high cost of metals for catalyst active species hinder its successful commercialisation (Rodriguez *et al*., 2014). Platinum (Pt) is the most active specie for the methanol electro-oxidation reaction but it is very scarce and expensive. In addition, during the methanol electro-oxidation reaction, carbon monoxide (CO) is produced as a reaction intermediate, which poisons the Pt catalyst. In order to overcome the Pt catalyst poisoning by the CO, the Pt has been alloyed with Ruthenium (Ru) to form Pt-Ru electro-catalyst, which has proven to be very active due to bi-functional mechanism and ligand electronics effect. Unfortunately, Ru is also costly (Magaji *et al*., 2019).

In recent years, researchers have deployed different strategies to reduce the cost of using only Pt or Pt-Ru as an electro-catalyst by introducing a low-cost transition metal active specie (s) as a promoter *(*Feng *et al.,* 2019*;* Barim *et al.*, 2020; Luo *et al.*, 2023). The incorporation of a transition metal in a Pt alloy alters the Pt 5d band vacancy and Pt-Pt interatomic distance. This leads to a downshift of the d-band center and weakened binding energy for oxygenated intermediates. The weakened adsorption of reaction intermediates tends to lower the activation energy for the oxygen reduction reaction, which enhances the performance of the electro-catalyst (Wang and Spendelow, 2021).

Cobalt (Co) is one of the promising transition metals being used because it has shown high synergistic catalytic activity. It has superior half wave potential, low catalyst cost and better OH resistance. Consequently, Pt-Co bi-metallic catalysts have been reported to display high performance for methanol electro-oxidation reaction *(*Amin *et. al.,* 2011, Huajie *et al.*, 2012, Magaji *et al*., 2019 and Heizmann *et al*., 2023). Despite its high performance, the Pt-Co bimetallic catalysts can further be improved to enhance durability and performance so as to meet market specifications. Therefore, more effective methods to customize the features of Pt-Co catalysts need to be developed (Wang and Spendelow, 2021).

Another approach of reducing the consumption of Pt and enhancing the catalytic activity of Pt-Co is the use of high surface area support material. Graphene, a two dimensional one-atom thick planar sheet of sp^2 bonded carbon atom, having a thickness of 0.34 nm has been proven to be a good support material due to its high specific surface area (2600 m^2/g), good electrical, thermal, mechanical and optical properties (Antolini 2012; Huajie *et al*., 2012, Jablonskienė *et al*., 2015, Li *et al*., 2022). However, despite its excellent properties as a catalyst support material, graphene has shortcomings that affect performance of the catalyst. The restacking of exfoliated graphene layers through Vander-Waals force and $\pi - \pi$ interaction between the layers lead to decrease in its electrical and mechanical properties (Huang and Wang, 2014). In addition, aggregation of graphene layers during Membrane Electrode Assembly (MEA) fabrication through the Vander-Waals force and $\pi - \pi$ interactions leads to decrease in specific surface area, low conductivity and decrease in catalytic activity of graphene supported catalyst (Antolini, 2012).

However, use of modified graphene as a support material is predicted to eliminate or drastically reduce the restacking of graphene layers and thus enhance the catalyst performance. Therefore, in this work, Pt-Co/rGO electro-catalysts were synthesized and characterized in order to ascertain its potential for the methanol electro-oxidation reaction.

2.0 MATERIALS AND METHODS

Analytical grade hexachloroplatinic (IV) hexahydrate ($H_2PtCl_6.6H_2O$) and cobalt (II) nitrate hexahydrate $Co(NO_3)_2.6H_2O$ precursors, ethylene glygol, sulphuric acid, phosphoric acid, hydrogen peroxide, sodium hydroxide, potassium permanganate and sodium borohydrate were procured from Cardinal Scientific Supplies, Ltd., Zaria, Nigeria.

The Pt-Co/rGO electro-catalysts were synthesized using reduced graphene oxide (rGO) as a support material. Graphene oxide was prepared from graphite by the modified Hummers' method. Typically, 20 g of graphite and concentrated H_2SO_4 (460 ml) were mixed in a beaker with vigorous magnetic stirring. Next, 60 g of $KMnO_4$ was slowly added to the beaker and the mixture was kept below 15℃ . The mixture was then stirred at 35℃ until its colour changed to brown and then diluted with 750 ml deionized (DI) water and kept below 90℃ while stirring. Then, the beaker was sealed and kept at 100℃ with vigorous stirring for 30 min. Thereafter, 20% H_2O_2 was added slowly. The mixture was washed with water, acetone, and 10% HCl solution in that order to remove residual metal ions and the sample was heated in an oven at 90℃ for 12 h to produce the graphene oxide powder (Nuengmatcha *et al*., 2016). Then, graphene oxide slurry was formed and mixed with 200 ml of distilled water and irradiated for 15 min. at 50 ℃ using an ultrasonic technique, filtered and dried at 80 ℃ for 40 h to obtain the reduced graphene oxide (rGO). Required amount of the $H_2PtCl_6.6H_2O$ was dissolved in 80 ml of ethylene glygol. Another 80 ml of the ethylene glygol was used to dissolve the Co $(NO_3)_2.6H_2O$ and then added drop wise into the mixture containing $H_2PtCl_6.6H_2O$.

Then the mixture containing the metal precursors and ethylene glygol was added drop-wise into the rGO solution and stirred for 1 hr. The whole mixture was then heated at 120 ℃ and kept at this temperature for 2 hr. under stirring. The final product was filtered and washed 3 times with ethanol, followed by distilled water to remove any residual ions and dried in an oven at 100℃ to produce the Pt-Co/rGO electro-catalysts (Yu *et al*.,2013).

3.0 CHARACTERIZATION OF THE SUPPORT MATERIAL AND THE ELECTRO-CATALYSTS

X-ray diffractograms

X-ray diffractograms (XRD) were obtained by PAN Analytical diffractometer equipment using Cu-Kα as the radiation source (λ = 0.15056 nm) operating under a voltage of 45 kV and current of 25 mA. The diffraction angle (2θ) was varied from 0 – 90.

SEM-EDX Analysis

The surface morphology of the graphene oxide and the developed electro-catalysts was studied using the Phenom Pro-X scanning electron microscope. The elemental compositions of the electro-catalysts were determined by the Energy Dispersive X-ray.

BET

Nitrogen adsorption at 77 K was carried out using Quantachrome Novawim Instrument to obtain the adsorption isotherms of the samples. The specific surface area of the samples were determined using the nitrogen adsorption data in relative pressure range from 0.05 – 0.3 via Brunauer-Emmett-Teller method. All the samples were out-gassed at 250ºC for 3 h prior to the analysis.

4.0 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns that were obtained for the graphite and graphene oxide materials. There was a sharp peak for the graphite material around 2θ = 26.5º confirming that the graphite material used was mainly a carbonaceous material. The peak can be ascribed to the hexagonal graphite structures of carbon (002), (JCPDS card No. 41-1487).

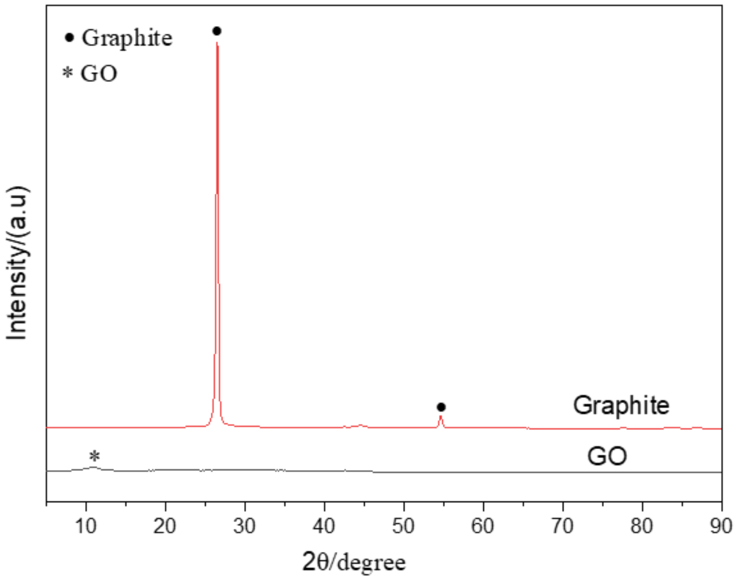

Figure 1: XRD Patterns of the graphene and graphene oxide materials

Figure 2 shows the XRD patterns obtained for the developed electro-catalyst samples using the PAN Analytical diffractometer equipment with Cu-Kα as the radiation source (λ = 0.15056 nm) operating under a voltage of 45 kV and current of 25 mA. The diffraction angle (2θ) was varied from 0 – 90º.

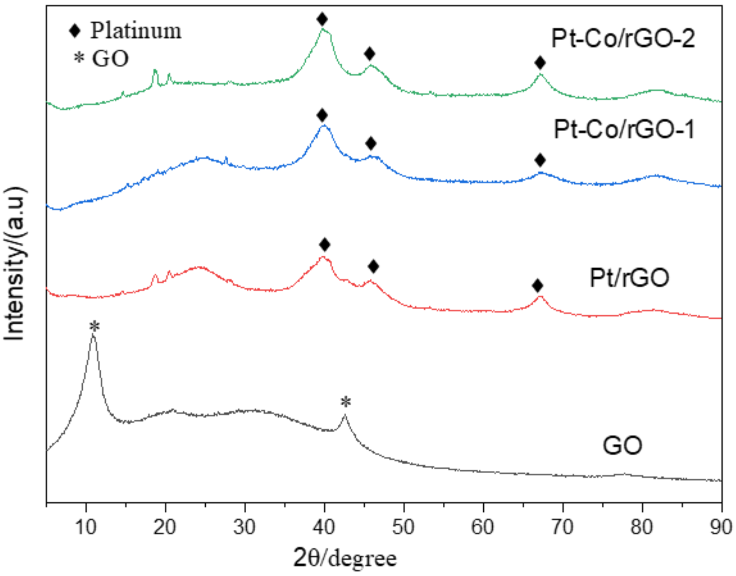

Figure 2: XRD Patterns of the developed electro-catalysts materials

The pattern of the Pt-Co/rGO showed diffraction peaks of (111), (200) and (220) (JCPDS Card 4-802) at 2θ values of 40º, 46º and 68º, respectively. The peaks confirmed the presence of the Pt metal active species in the face-centred cubic (fcc) structure. This corresponds to a similar observation by Chen *et. al*., 2015. Thus, the XRD patterns confirmed the bimetallic alloy nature of the Pt-Co/rGO electro-catalysts. Compared to the standard face-centered cubic (fcc) platinum, the dominant (111) and (200) plane peaks are expanded indicating a lattice contraction due to the formation of the alloy.

Figures 3 – 8 show the Scanning Electron Microscopic (SEM) images while Tables 1 -3 show the elemental composition obtained from the Energy Dispersive X-ray (EDX) for the developed Pt/rGO, Pt-Co/rGO-1 and Pt-Co/rGO-2 electro-catalysts. The results of the elemental composition confirmed that 25 – 30% of active species were used for the formulation of the Pt-Co/rGO-1 and Pt-Co/rGO-2 electro-catalysts. During the practical formulation, 30% Pt was used for the Pt/rGO, 10% Pt and 20% Co were used for the Pt-Co/rGO-1 while 15% Pt and 15% Co were used for the Pt-Co/rGO-2. These fall within the range being used for the formulation of high performance electro-catalysts.

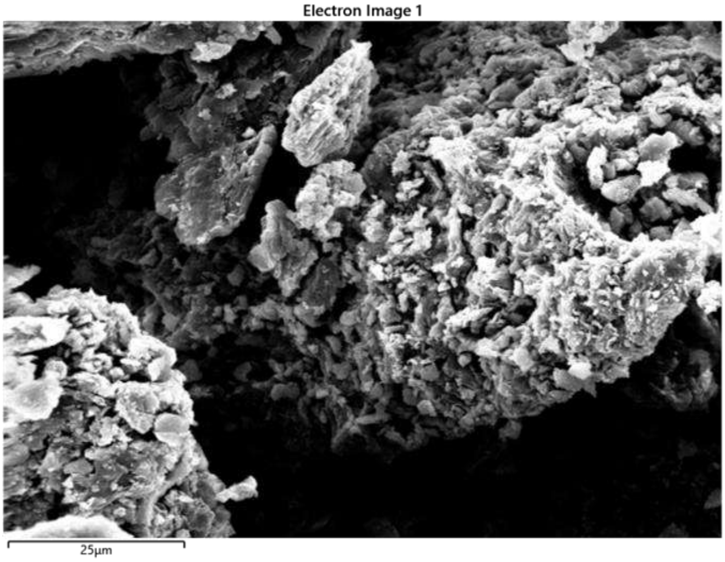

Figure 3: SEM Image for the Pt/rGO electro catalyst

Table 1: Elemental composition of the Pt/rGO electro-catalyst

Element	**Weight %**	**Atomic %**
C	36.97	58.10
O	34.60	33.32
Pt	28.43	8.58
Total	100.00	100.00

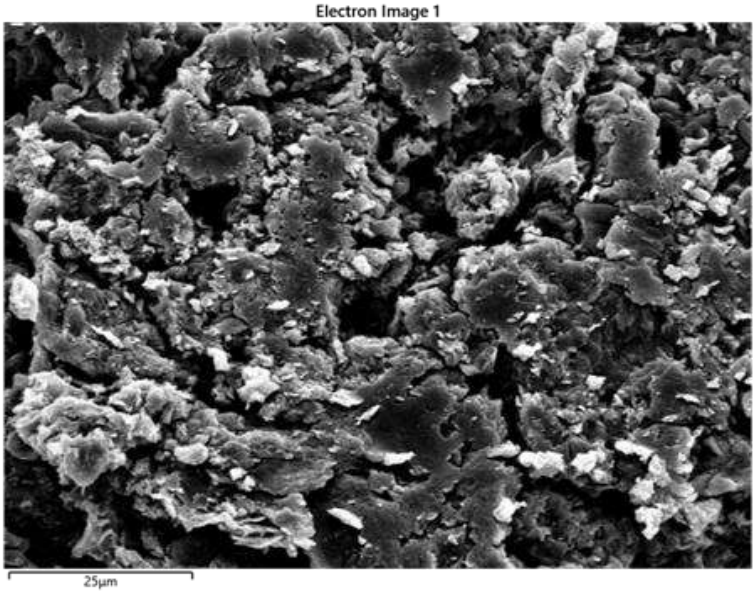

Figure 4: SEM Image for the Pt-Co/rGO-1 electro catalyst

Table 2: Elemental composition of the Pt-Co/rGO-1 electro-catalyst

Element	**Weight %**	**Atomic %**
C	44.69	62.61
O	30.25	31.82
Co	17.23	4.08
Pt	7.83	1.49
Total	100.00	100.00

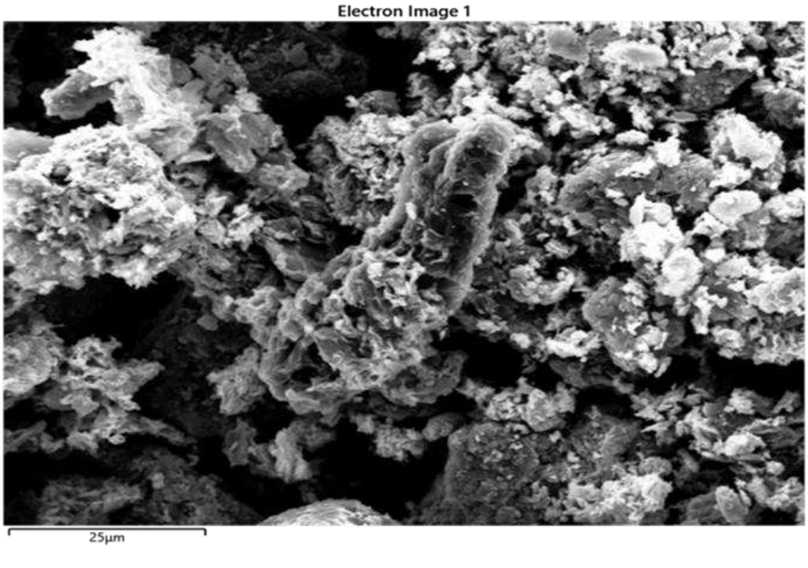

Figure 5: SEM Image for the Pt-Co/rGO-1 electro catalyst

Table 3: Elemental composition of the Pt-Co/rGO-2 electro-catalyst

Element	**Weight %**	**Atomic %**
C	40.85	61.86
O	30.09	33.21
Co	15.65	3.29
Pt	13.42	1.64
Total	100.00	100.00

Figure 6 shows the N_2 Adsorption curves for the developed electro-catalysts while the N_2 adsorption/desorption for the analysis of the catalyst pore structure is shown on Table 4. The data is used to determine the BET specific surface area, pore volume and pore diameter. The results indicate high specific surface area (41.1435 m²/g) for the reduced graphene oxide, which enables excellent dispersion of active species that will lead to good electro-catalysts performance.

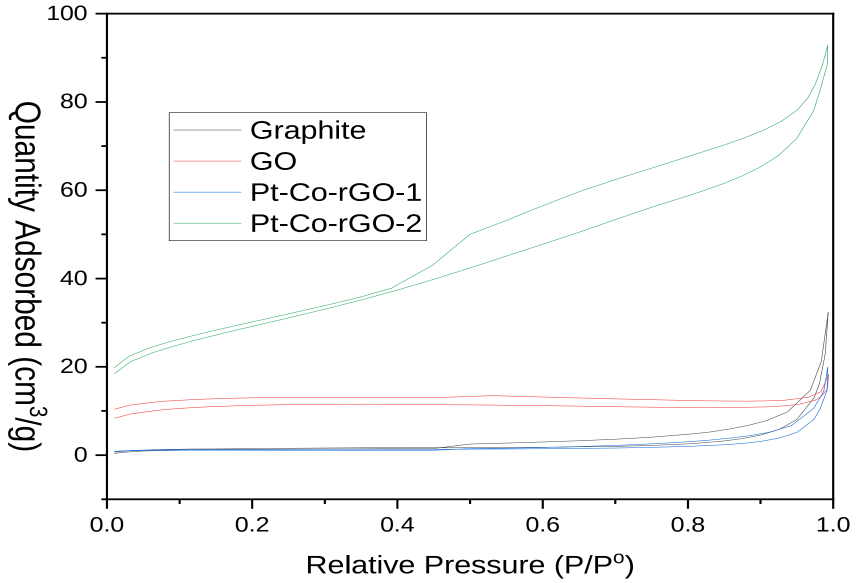

Figure 6: N_2 adsorption/desorption curves for the developed electro-catalysts

Table 4: N_2 adsorption/desorption for the analysis of the catalyst pore structure

Samples	**S_{BET}(m²/g)**	**S_{Micro}(m²/g)**	**V_{Pore}(cm³/g)**	**V_{micro}(cm³/g)**	**Pore Size(nm)**
Graphite	5.5293	2.0582	0.019998	0.000784	24.0147
Reduced graphene oxide	41.1435	26.1687	0.019289	0.010876	84.7204
Pt-Co/rGO-1	4.8245	3.4874	0.012589	0.001417	25.7559

Pt-Co/rGO-2	4.7682	10.6486	0.120465	0.004812	23.6473

5.0 CONCLUSION

High specific surface area (41.1435 m²/g) reduced graphene oxide (rGO) was successfully synthesized using graphite powder. The rGO was characterized for use as a support material in the formulation of Pt-Co/rGO electro-catalysts. The developed Pt-Co/rGO electro-catalysts were characterized using SEM, EDX, XRD and BET. Based on the results presented, the Pt-Co/rGO electro-catalysts have potential to be used for the methanol electro-oxidation reaction at the anode of a Direct Methanol Fuel Cell.

6.0 ACKNOWLEDGEMENT

The support of the Tertiary Education Trust Fund (TETFund) through the IBR grant - (TETF/DR&D/UNI/ZARIA/IBR/2020/VOL.1/47) is highly appreciated.

7.0 REFERENCES

C. Wang and J. S. Spendelow (2021). Recent developments in Pt-Co catalysts for PEM fuel cells. *Current Opinion in Electrochemistry*, vol. 28, https://doi.org/10.1016/j.coelec.2021.100715

E. Antolini, (2012). Graphene as a new carbon support for low-temperature fuel cell catalysts. *Applied Catalysis B: Environmental*, vol. 123–124, pp52–68. https://doi.org/10.1016/j.apcatb.2012.04.022

H. Huajie, S. U. N. Dongping, & W. Xin, (2012). PtCo alloy nanoparticles supported on graphene nanosheets with high performance for methanol oxidation. *Chin Sci Bull*, vol. 57(23), pp3071–3079. https://doi.org/10.1007/s11434-012-5327-4

J. Jablonskienė, V. Kepenienė, A. Matusevičiūtė, A. Drabavičius, A., L. Tamašauskaitė-tamašiūnaitė, (2015). Synthesis , characterization and properties of the graphene supported platinum – cobalt nanocatalysts. *ECS Meeting Abstracts*, MA2015-03(3):631-631

J. R. Rodriguez, R. M. Félix, E. A. Reynoso, Y. Gochi-Ponce, Y. V. Gómez, S. F. Moyado, & G. Alonso-Núñez, (2014). Synthesis of Pt and Pt-Fe nanoparticles supported on MWCNTs used as electrocatalysts in the methanol oxidation reaction. *Journal of Energy Chemistry*, vol. *23*(4), pp483–490. https://doi.org/10.1016/S2095-4956(14)60175-3

P. A. Heizmann, H. Nguyen, M. V. Holst, A. Fischbach, M. Kostelec, F. J. G. L. de Marjan Bele, L. Pavko, T. Đuki, M. Sala, F. Ruiz-Zepeda, C. Klose, M. Gatalo, N. Hodnik, S.

Vierrath and M. Breitwieser (2023). Alternative and facile production pathway towards obtaining high surface area PtCo/C intermetallic catalysts for improved PEM fuel cell performance, *Royal Society of Chemistry (RSC) Advances*.,vol.,13, pp4601 -4611.

P. Nuengmatcha, S. Chanthai, R. Mahachai, and W. Oh (2016). Visible light-driven photocatalytic degradation of rhodamine B and industrial dyes (texbrite BAC-L and texbrite NFW-L) by ZnO-graphene. *Journal of Environmental Chemical Engineering*, vol. 4, no. 2, pp. 2170–2177, doi: 10.1016/j.jece.2016.03.045.

R. S. Amin, K. M. El-Khatib, R. M. A. Hameed, E. R. Souaya, and M. A. Etman (2011). Synthesis of Pt-Co nanoparticles on multi-walled carbon nanotubes for methanol oxidation in H_2SO_4 solution. *Applied Catalysis A General.*, vol. 407, no. 1–2, pp. 195–203, doi: 10.1016/j.apcata.2011.08.045.

S. B. Barim, S. E. Bozbag, B. Deljoo, M. Aindow and C. Erkey (2020). *Fuel Cells*, vol. 20(3), pp285–299.

S. Li, X. Yan, M. Shi, ^{P}. Wei, H. Lu, ^{Z}. Zhang, Y. Zhang and Y. Li (2022). Electrodeposition of Pt-Ni nanoparticles on graphene as an electrocatalyst for oxygen reduction reaction. *Frontiers in Chemistry*, doi: 10.3389/fchem.2022.1061838

S. Magaji, A. Hamza, & B. Mukhtar,(2019). Synthesis and characterization of platinum-cobalt supported on activated carbon electrocatalys. *Nigerian Journal of Engineering*, vol. *26*(2), pp90–98.

S. Yu, Q. Liu, W. Yang, K. Han, Z. Wang, and H. Zhu (2013). Graphene – CeO_2 hybrid support for Pt nanoparticles as potential electrocatalyst for direct methanol fuel cells. *Electrochimica Acta*, vol. 94, pp. 245–251, doi: 10.1016/j.electacta.2013.01.149.

W. Luo, Y. Jiang, M. Wang, D. Lu, X. Sun and H. Zhang (2023). Design strategies of Pt-based electrocatalysts and tolerance strategies in fuel cells: a review. *Royal Society of Chemistry (RSC) Advances*, vol., 13, pp4803–4822

Y. Y. Feng, H. S. Hu, G. H. Song, R. J. Liu, D. N. Peng, &D. S. Kong, (2019). Promotion effects of CeO_2 with different morphologies to Pt catalyst toward methanol electrooxidation reaction. *Journal of Alloys and Compounds*, vol. *798*, pp706–713. https://doi.org/10.1016/j.jallcom.2019.05.287