Development of Graphene based bimetallic (Co-Ni) electro-catalyst for Fuel cell applications

By

Ehtsham Sarwar

Reg. # NUST201463529MCES64114F

Session 2014-16

Supervised by

Dr. Naseem Iqbal

A Thesis Submitted to the U.S. Pakistan Center for Advanced Studies in Energy in partial fulfillment of the requirements for the degree of

MASTERS of SCIENCE in
ENERGY SYSTEMS ENGINEERING

U.S. Pakistan Center for Advanced Studies in Energy (USPCAS-E)
National University of Sciences and Technology (NUST)
H-12, Islamabad 44000, Pakistan
March 2017

THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS/MPhil thesis written by **Mr. Ehtsham Sarwar**, (Registration No. NUST201463529MCES64114F) of USPCAS-E has been vetted by undersigned, found complete in all respects as per NUST Statues/Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for award of MS/MPhil degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have also been incorporated in the said thesis.

Signature: ______________________________

Name of Supervisor ________________________

Date: ________________________

Signature (HoD): ________________________

Date: ____________________________________

Signature (Dean/Principal): __________________

Date: ____________________________________

Certificate

This is to certify that work in this thesis has been carried out by **Mr. Ehtsham Sarwar** and completed under my supervision in FT Synthesis Laboratory, USPCAS-E, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

Supervisor:
____
Dr. Naseem Iqbal
USPCAS-E
NUST, Islamabad

GEC member # 1:
____
Dr. Zuhair S Khan
USPCAS-E
NUST, Islamabad

GEC member # 2:
____
Dr. Eng. Muhammad Zubair
USPCAS-E
NUST, Islamabad

GEC member # 3:
____
Dr. Nadia Shahzad
USPCAS-E
NUST, Islamabad

HoD-USPCAS-E
____
Dr. Zuhair S Khan
USPCAS-E
NUST, Islamabad

Principal/ Dean
____
Dr. M. Bilal Khan
USPCAS-E
NUST, Islamabad

Abstract

Carbon black was used as a support material for fuel cell but their properties doesn’t fulfil the requirements for the better electro-catalytic activity. However, graphene can overcome the main problem facing the non-precious electro-catalysts; low electro-catalytic activity. Usually platinum based electrode materials were used in direct methanol fuel cells but its commercialization becomes limited due to its high cost. In this paper the electro-catalytic oxidation of methanol is studied on the non-noble catalysts Ni-Co/graphene. The bimetallic electro-catalyst was prepared with different Co-Ni ratios such as Co_1-Ni_1 (0.5 mmol of cobalt and 0.5 mmol of nickel), Co_1-Ni_2 (0.3 mmol of cobalt and 0.6 mmol of nickel) and Co_1-Ni_4 (0.2 mmol of cobalt and 0.8 mmol of nickel) by using simple solution synthesis method. The synthesized materials are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electro-catalytic activity of Ni-Co/graphene for methanol oxidation was investigated by cyclic voltammetry (CV) for DMFCs application.

Keywords: DMFCs; Graphene; Electro-catalyst; Electro-catalytic activity; Cyclic voltammetry.

Acknowledgements

I would like to express my sincerest gratitude to my thesis supervisor Dr. Naseem Iqbal, whose technical knowledge has been a cornerstone in completing my work. His suggestions and guidance has been a constant source of motivation and learning during my research period.

I would also like to extend my gratitude to Dr. M. Bilal Khan, Dr. Zuhair S Khan, Dr. Nadia Shahzad and Dr. Eng. Muhammad Zubair, US Pakistan Center for Advanced Studies in Energy, USPCAS-E NUST. I would like to mention the effective cooperation of Dr. Safeer Ahmed, Department of Chemistry, QAU.

Finally, I owe my deepest gratitude to my friends and family members whose unconditional love, absolute affection, infinite trust, and endless confidence inspired me to complete my work.

Table of Contents

Chapter 1

List of Figures

List of Tables

List of Journals / Conference papers

Conference Papers:

Ehtsham Sarwar, M Irfan Raza and Naseem Iqbal, ‘‘Graphene based electro-catalysts for DMFCs,” in 3rd. International conference on Innovative Engineering Technologies (ICIET'2016) August 5-6, 2016 Bangkok (Thailand) pp. 96–100. http://dx.doi.org/10.15242/IIE.E0816. (Attached to Annexure II)

Ehtsham Sarwar, M Irfan Raza and Naseem Iqbal, ‘‘Development of Co-Ni/Graphene based bimetallic electro-catalyst for methanol oxidation in Proceedings of The IRES International Conference, Pune, India, 25th-26th January 2017, ISBN: 978-93-86083-34-0. (Attached to Annexure I)

List of abbreviations

Pt	Platinum
Ni	Nickel
Co	Cobalt
PEMFC	Polymer Electrolyte Membrane fuel cell
AFC	Alkaline fuel cell
MFC	Microbial fuel cell
MCFC	Molten carbonate fuel cell
PAFC	Phosphoric acid fuel cell
DMFC	Direct methanol fuel cell
GCE	Glassy carbon electrode
GO	Graphene oxide
CV	Cyclic Voltammetry
XRD	X – ray diffraction
SEM	Scanning electron microscopy

Chapter 1

Introduction

1.1 Energy crisis and renewable resources

In 2013 total energy produced worldwide was dominated by fossil fuels about 86.59 % which includes oil, natural gas and coal with the percentage of 32.87 % by oil, 23.72 % by natural gas and 30 % by coal respectively [1]. Due to increase in the energy demands with the passage of time, continuous and readily depletion of fossil fuels with the increase in the concentration of greenhouse gases like sulfur oxide (SO_x), nitrogen oxide (NO_x) and carbon-dioxide (CO_2) encourages the researchers to focus on the development of alternative and cleaner energy resources**.** Renewable energy resources include solar thermal and PV, wind energy, biomass, geothermal, biofuels and fuel cells. Today fuel cell is considered to be efficient, non-polluting, environmental friendly, higher energy efficiencies and higher current densities comparable to the other current systems [2].

1.2 Fuel Cell

In 1839, the Welsh chemical-physicist and patent lawyer William Robert Grove proves that an electrochemical reaction between the hydrogen (H_2) and oxygen O_2 produce an electric current. The Ludwig Mond a British chemist and Charles Langer used coal as fuel obtaining 20 Am^{-2} at 0.73 volt and named it as fuel cell [3]. At the end of 1950s NASA uses fuel cell for space missions [4]. Similarly, with the passage of time, the use of fuel cells in electric vehicles is proposed and since 2007 they are commercialized vehicles e suitable for public transport and power Fuel cells can be utilized in the range 1 W to 10 KW for personal computers, cell phones and other electric equipment's. Similarly, fuel cells in the range 1-100 KW are suitable for public transport and power vehicles purposes and 1-10 MW fuel cells can be used in power systems for energy [3]. Fuel cell is a device that converts chemical energy of fuel into electricity through the chemical reaction. Fuel cells are different from the batteries because they need fuel continuously and oxygen or air in order to maintain the chemical reaction, while in case of batteries chemicals present in the battery react with each other to generate electromotive force. Fuel cells can produce electricity as long as fuel and oxygen or air is supplied as an input. Fuel cells prove a more efficient, cleaner and most flexible energy conversion from chemical to electrical. Generally, fuel cell is consisting of an anode, cathode and an electrolyte which is sandwiched between the anode and cathode. There are many types of fuel cells available differ in their operating temperature, electrical efficiencies, power outputs and typical applications [1]. There is no combusting of fuel in the fuel cells, so that no harmful emissions are generated by the fuel cells. Which results in production of power in the absence of sulfur oxide (SOx), nitrogen oxide (NOx) and particulate matter (PM**)** [5]. Fuel cells combine advantages of both batteries as well as engines. Fuel cells have no moving parts, mechanically ideal and can be all solid state. As there are no moving parts in fuel cells so they are silent [6]. Fuel cell produces zero pollutants as compare to the heat engines. Producing electricity from the heat engine is a multi-step process while fuel cells produces electrical work directly from the chemical energy. Main types of fuel cells are Polymer electrolyte membrane fuel cells (PEMFCs), Alkaline fuel cells (AFCs), Molten carbonate fuel cells (MCFCs), Phosphoric acid fuel cells (PAFCs), Microbial fuel cells (MFCs), Solid oxide fuel cells (SOFCs) and Direct methanol fuel cells (DMFCs**)** [1].

1.3 Types of Fuel Cells

1.3.1 Polymer Electrolyte Membrane Fuel Cells

A PEMFC converts the chemical energy during the electrochemical reaction of hydrogen (H_2) and oxygen (O_2) to electrical energy.

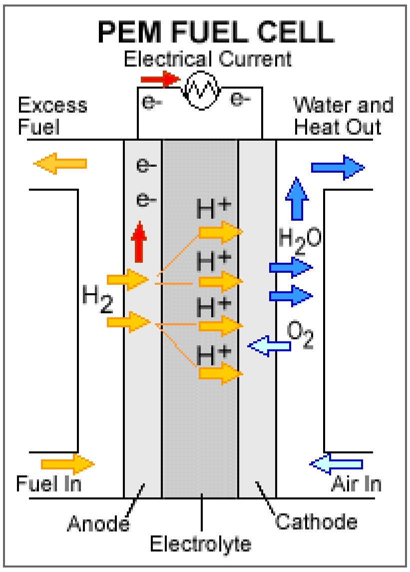


Figure 1.1: Schematic representation of PEMFC [7].

At the Anode:

$H_2 \longrightarrow 2\,H^+ + 2e^-$

At the Cathode:

$\frac{1}{2}\,O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

The overall reaction in the fuel cell produces heat, water and electrical works. The major applications of polymer electrolyte membrane fuel cells are related to the transportation as well as distributed/stationary and portable power generation due to its high-power density and excellent characteristics. PEM fuel cell cannot be commercialized world-wide due to its high cost and durability problems [8].

1.3.2 Alkaline fuel cells

The fuel cell produces power through a redox reaction between hydrogen (H_2) and oxygen (O_2).

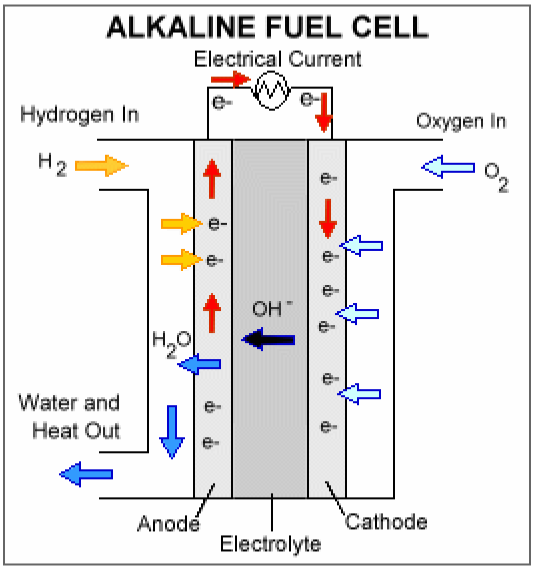


Figure 1.2: Schematic Representation of AFC [7].

At the anode:

$$2H_2 + 4OH^- \longrightarrow 4H_20 + 4e^-$$

At the cathode:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

In the start, Alkaline fuel cells used liquid electrolytes like solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH) or diluted acid [9]. AFC is the first type which is used in the US space program to produce water on-board spacecraft and electrical energy. Recently AFCs have been developed that use a polymer membrane as an electrolyte. AFCs are closely related to the polymer electrolyte membrane fuel cells. Alkaline fuel cell has high performance due to the rate at which electrochemical reaction takes place in the cell. AFCs shows efficiency greater than 60 % in space applications [7].

1.3.3 Molten carbonate fuel cells

Like the other fuel cells, the working principle of the molten carbonate fuel cell is based on the indirect combination of hydrogen (H_2) and oxygen (O_2) to water (H_2O) through the electron carrying electrolyte [10].

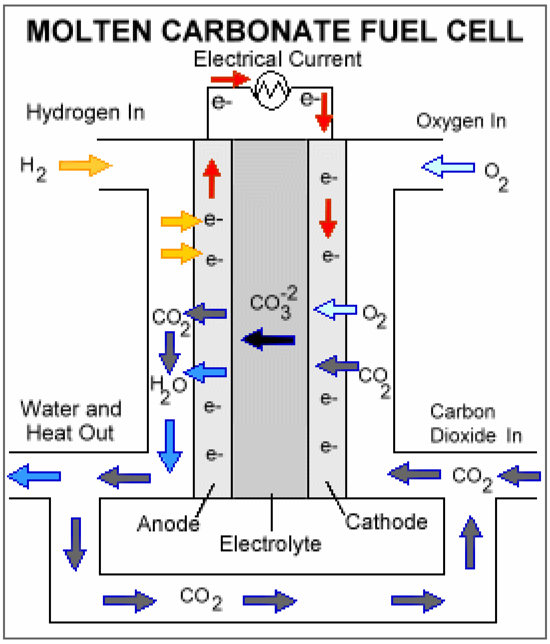


Figure 1.3: Schematic Representation of MCFC [7].

Reactions

Internal Reformer:

$CH_4 + H_20 = 3H_2 + CO$

At the anode:

$H_2 + CO_3^{=} = H_2O + CO_2 + 2e^-$

At the cathode:

$\frac{1}{2} O_2 + CO_2 + 2e^- = CO_3^{=}$

In the next few years' significant reduction in the capital cost of MCFC is expected [10]. Molten carbonate fuel cells are developed for coal-based and natural gas power plants for industrial purpose, electrical utility and for military applications also**.** Unlike alkaline fuel cell and conventional polymer electrolyte membrane fuel cell, molten carbonate fuel cell doesn't require any external reformer to convert fuel such as biogas and natural gas to hydrogen [7].

1.3.4 Phosphoric acid fuel cells

Phosphoric acid fuel cells use liquid phosphoric acid as an electrolyte. PAFCs are the first fuel cells to be commercialized**.** In the PAFC hydrogen is provided to the anode side while the air is provided to the cathode side, where oxygen reacts with the protons and electrons coming from the external load and electrolyte [11].

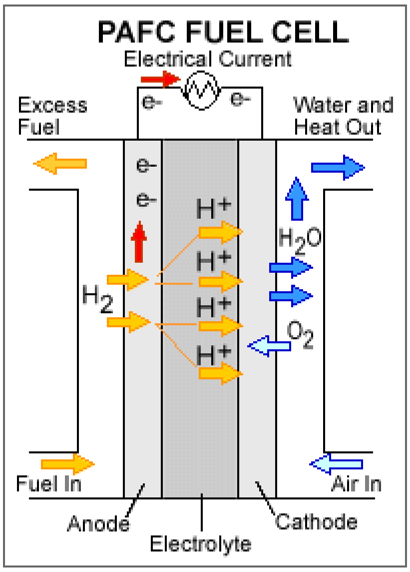


Figure 1.4: Schematic Representation of PAFC [7].

At the anode:

$$2H_2\,(g) \longrightarrow 4H^+ + 4e^-$$

At the cathode:

$$O_2\,(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The first phosphoric acid fuel cell power plant was installed in the 1970s, and now there are 500 power plants in the world. Phosphoric acid fuel has improved performance, cost and stability significantly in the recent years. That's why PAFCs are considered as a good candidate for the stationary applications [11].

1.3.5 Microbial fuel cells

Microbial fuel cell also known as biological fuel cell is a bio-electrochemical system that basically drives current by using bacteria. Microbial fuel cells are similar to the any other battery or fuel cell type having anode and cathode connecting through the external wire, but MFCs use organic substance as a fuel on the anode side in order to produce electricity. Microbial fuel cells are attractive for power generation applications that require low power [12].

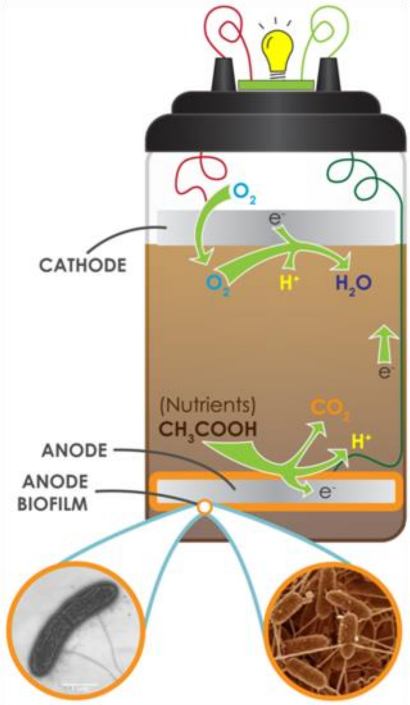


Figure 1.5: Schematic Representation of Soil based MFC [13].

1.3.6 Solid oxide fuel cells

Solid oxide fuel cell is one of the most efficient and environmental friendly fuel cell type that that generates power from natural gas, hydrogen and other renewable fuels [14]. Solid oxide fuel cell has ceramic or solid oxide electrolyte. Main advantages of solid oxide fuel cell include low cost, low emissions, fuel flexibility, high efficiency, and long term stability.

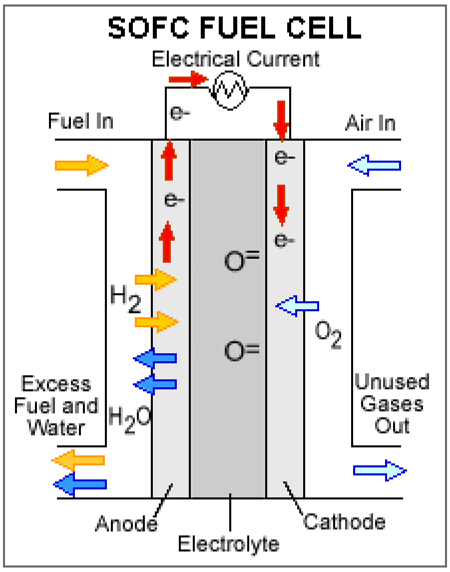


Figure 1.6: Schematic Representation of SOFC [7]

At the anode:

$H_2 + O_2^- \longrightarrow H_20 + 2e^-$

At the cathode:

$½ O_2 + 2e^- \longrightarrow O_2^-$

Solid oxide fuel cells don’t require precious-metal catalyst because they are operated at high temperature, therefore reducing cost [7]**.** Solid oxide fuel cells can also be integrated with a gas turbine in order to form large scale hybrid system**.** Due to high operating temperature, there are some issues like mechanical and chemical stability as well as longer start -up times [15].

1.3.7 Direct Methanol Fuel cells

Many researchers have reported that direct methanol fuel cell is an alternative to rechargeable battery. DMFCs are suitable for portable energy applications. Basically, DMFCs is a further development of the hydrogen PEMFC that is suitable for portable electronic and vehicular applications [16].

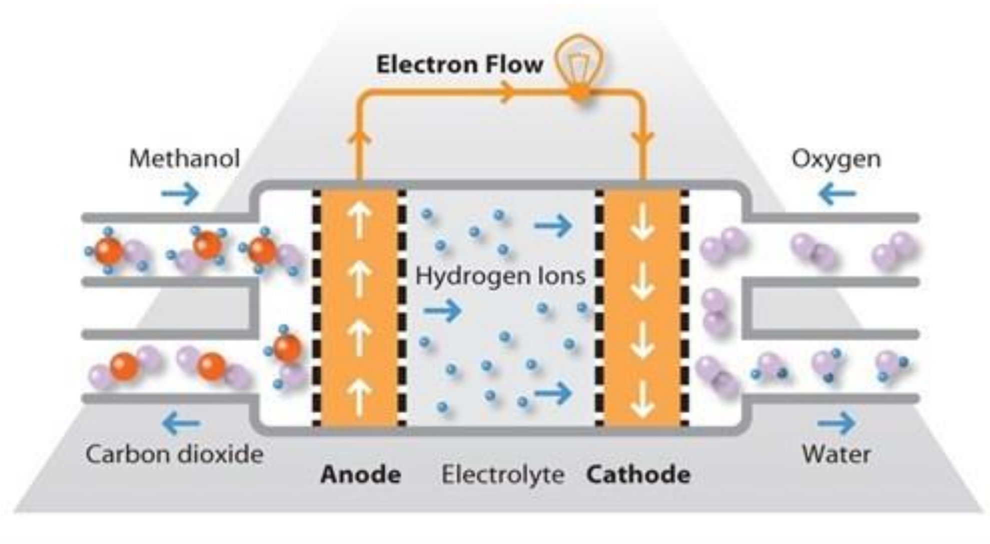


Figure 1.7: Schematic representation of DMFCs [17]

In Direct methanol fuel cells, methanol is electro-oxidized to carbon-dioxide through the reaction at anode while at the cathode oxygen (usually air) is reduced to H_2O or steam.

At the Anode:

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

At the Cathode:

$$3/2\ O_2 + 6e^- + 6H^+ \longrightarrow 3\ H_2O$$

Transport and supply of methanol to the public places is also easier. There are no storage problems of fuel in direct methanol fuel cells. As the efficiency of direct methanol fuel cells is low, so they are suitable for portable applications where power density and energy are more important as compare to the efficiency [16].

1.3.7.1 Current Issues in DMFCs

Every component in direct methanol fuel cell has its own challenges, scientists and researchers are trying to overcome these problems. In DMFCs, methanol crossover is the main problem. Although high concentration of methanol provides higher energy density but at the same time it also causes methanol crossover to the electrolyte membrane which results in mix potential at the cathode side which leads to the low cell performance. However, development of new proton conducting membranes can reduce the problem of methanol crossover [18]. Management of heat is another problem in direct methanol fuel cell. As methanol crossover increases with the increased methanol concentration, thus increasing the cell temperature which enhanced reaction kinetics at both cathode and anode. Similarly, direct methanol fuel cell also faces slow reaction kinetics of methanol electrooxidation. In direct methanol fuel cells, anode suffers high activation over potential because of the slow kinetics of methanol oxidation reaction. Slow reaction kinetics of methanol oxidation reaction limits the rate electrode reactions, which decreases the cell voltage and affects the voltage efficiency of the system. Generally, platinum based electro-catalyst is used as an anodic material. Direct methanol fuel cell needs higher loading catalyst, in some cases more than ten times as compare to the H_2-fed PEMFCs due to the methanol crossover at the cathode side and slow kinetics of methanol electrooxidation reaction. But platinum-based electro-catalyst is high in cost which limits its commercialization. So, in order to replace platinum, it is very important to develop new anodic materials to direct methanol fuel cells more effective in terms of overall efficiency [19].

Table: 1.1 Detailed comparison of fuel cell technologies [1], [6].

Type	PEMFC	DMFC	PAFC	AFC	MCFC	SOFC
Operating temperature	120ºC	50-180ºC	15-200ºC	60-220ºC	650ºC	600-1000ºC
Electrolyte	Polymer membrane (Perfluoro sulfonic acid)	Nafion	Liquid H_3PO_4 soaked in a porous matrix	Alkaline polymer membrane	Molten carbonate soaked in a porous matrix	Ceramic (Yttria-stabilized zirconia)
Fuel	Hydrogen	Methanol	Hydrogen		Hydrogen, methane and carbon monoxide	
Catalyst	Platinum	Platinum	Platinum	Platinum	Nickel	Perovskites
Efficiency	35% Stationary 60% Transportation		70% CHP unit 40% Electrical	60 %	90% CHP unit 60% Electrical	60%
Charge carrier	H^+			OH-	CO_3^{2-}	O^{2-}
Cell components	Carbon based	Carbon based (Graphite)	Carbon based		Stainless steel based	Ceramic Based
Applications	1.Transport purposes 2.Portable power 3.Distributed generation	1.Military 2.Laptops 3.Cell phones	Distributed Generation	Space and Military purposes	1.Distributed generation 2.Electric utility	1.Electric Utility 2.Auxiliary power
Advantages	1.Quick start-up 2.Low temperature 3.Solid electrolyte reduces corrosion	1.Methanol fuel is inexpensive 2.High energy density	Tolerance to fuel Impurities	1.High performance 2.Low cost Components	Use variety of catalyst Highly flexible	1.High flexibility 2.High efficiency 3.Solid electrolyte 4.Hybrid and GT cycle

1.4 Problem statement

In 2013 total energy produced worldwide was dominated by fossil fuels about 86.59 %. Usage of these fossil fuels (Coal, Natural gas and oil) produces a large number of carbon dioxide emissions (CO_2) and other emissions like SOx, NOx and formation of harmful particulate matter. So, in order to overcome these problems, it is very important to utilize alternate and renewable resources to meet our energy demands. Among the renewable energy resources fuel cell can provide us greener and renewable energy with almost zero emissions. Direct methanol fuel cell is a type of fuel cells, that is basically subcategory of PEMFC, in DMFC methanol is used as a fuel instead of hydrogen. DMFCs are useful because transport of methanol is easier, they are suitable for portable applications where energy and power density are more important than efficiency.

The main disadvantage of direct methanol fuel cell is its lower power density. The lower cell performance of the DMFCs is due to the poor kinetics of the electrode reactions. Platinum is usually used as an electrode material for the oxidation of DMFCs, but platinum is very expensive so its commercialization is not economical. So, in order to develop an alternate catalyst, researchers focus on development of non-noble metal catalyst, such as Nickel (Ni), Cobalt (Co), Lead (Pb) and Tungsten (W) to replace platinum and other noble metals to reduce the cost of catalyst. Secondly researchers focus on using high conductive materials as support, like mesoporous carbon, carbon nanotubes and graphene to improve efficiency of electro-catalyst for the oxidation of methanol.

1.5 Objectives

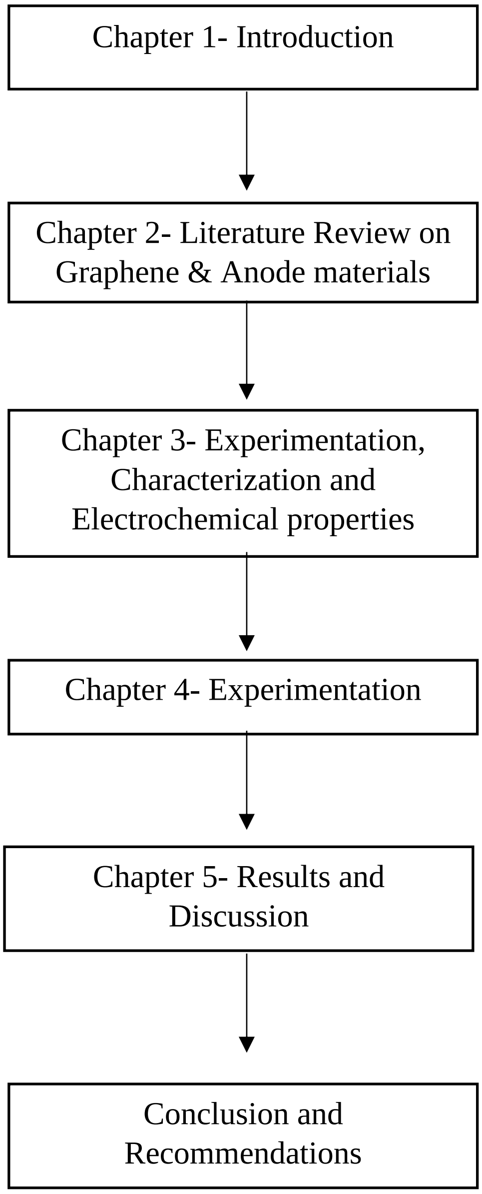
The objectives of this research were:

i. To synthesize graphene oxide (GO) and Co_xNi_y-decorated graphene electro-catalyst for the electrooxidation of Direct methanol fuel cells.
ii. To study the electrochemical properties of the prepared electro-catalyst.

Summary

Fuel cells are the type of renewable energy resources which converts chemical energy of fuel into electrical energy. There are various types of fuel cells differ from each other in terms of electrolyte, operating temperature, electrode materials and efficiency also. Fuel cell is known to produce greener and renewable energy with almost zero emissions. Each fuel cell has its own advantages and disadvantages.

Direct methanol fuel cell is very suitable for portable applications where energy and power density are more important than efficiency. Transport of methanol is also easier. Generally, platinum is an ideal electrode material for the oxidation of methanol but due to its high cost its commercialization is not effective. Direct methanol fuel cell can be utilized in order to meet world energy demands.



Figurative flow of the thesis.

References

[1] BP Energy Outlook 2035, 2014.

[2] Sharma, Surbhi, and Bruno G. Pollet. "Support materials for PEMFC and DMFC electrocatalysts—a review." Journal of Power Sources 208 (2012): 96-119.

[3] Lucia, Umberto. "Overview on fuel cells." Renewable and Sustainable Energy Reviews 30 (2014): 164-169.

[4] Sharaf, Omar Z., and Mehmet F. Orhan. "An overview of fuel cell technology: Fundamentals and applications." Renewable and Sustainable Energy Reviews 32 (2014): 810-853.

[5] http://californiahydrogen.org/sites/default/files/1117%20-%20Nielsen.pdf

[6] R. O'Hayre, S.W. Cha, W. Colella, F.B. Prinz, Fuel Cell Fundamentals, Wiley, 2009.

[7] https://energy.gov/eere/fuelcells/types-fuel-cells

[8] Wang, Yun, et al. "A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research." Applied Energy 88.4 (2011): 981-1007.

[9] Kordesch, Karl, et al. "Alkaline fuel cells applications." Journal of Power Sources 86.1 (2000): 162-165.

[10] Bischoff, Manfred. "Molten carbonate fuel cells: a high temperature fuel cell on the edge to commercialization." Journal of Power Sources 160.2 (2006): 842-845.

[11] Sammes, Nigel, Roberto Bove, and Knut Stahl. "Phosphoric acid fuel cells: Fundamentals and applications." Current opinion in solid state and materials science 8.5 (2004): 372-378.

[12] Oliveira, V. B., et al. "Overview on the developments of microbial fuel cells."Biochemical Engineering Journal 73 (2013): 53-64.

[13] https://en.wikipedia.org/wiki/Microbial_fuel_cell#/media/File:SoilMFC.png.

[14] Choudhury, Arnab, H. Chandra, and A. Arora. "Application of solid oxide fuel cell technology for power generation—A review." Renewable and Sustainable Energy Reviews 20 (2013): 430-442.

[15] Minh, Nguyen Q. "Solid oxide fuel cell technology—features and applications." Solid State Ionics 174.1 (2004): 271-277.

[16] Kamarudin, Siti Kartom, F. Achmad, and Wan Ramli Wan Daud. "Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices." International Journal of Hydrogen Energy 34.16 (2009): 6902-6916.

[17] http://www.fuelcelltoday.com/technologies

[18] Broussely, Michel, and Graham Archdale. "Li-ion batteries and portable power source prospects for the next 5–10 years." Journal of Power Sources 136.2 (2004): 386-394.

[19] Liu, Jing Hua, et al. "Highly-optimized membrane electrode assembly for direct methanol fuel cell prepared by sedimentation method." Journal of power sources 137.2 (2004): 222-227.

Chapter 2

Literature Review

2.1 Role of Electro-catalyst in Direct methanol fuel cells

Electro-catalyst is a catalyst that takes part in an electrochemical reaction. Electro-catalyst is a specific form of catalyst that basically function at electrode surface. Electro-catalyst can be homogeneous like a coordination complex or electro-catalyst can be heterogeneous like nanoparticles or platinum surface. Practically both electrodes (anode and cathode) are kinetically limited because of the irreversible nature of the reactions. Therefore, it has been observed that both the electrodes (anode and cathode) are suffer from large over potentials [1]. In a typical direct methanol fuel cell, CH_3OH will oxidize to carbon dioxide (CO_2) at the anode. But when oxidation reaction occurs, it results in the formation of carbon monoxide (CO) as an intermediate, which mostly adsorbs on the surface of platinum catalyst. So, that a potential that is much more anodic as compare to the thermodynamic value in DMFCs is required to have a reasonable reaction rate. Therefore, in direct methanol fuel cells both electrodes (anode and cathode) are suffer from kinetic losses, whereas in PEMFCs only the cathode is suffering from kinetic losses [2]. Therefore, various materials have been reported as an electrode material to lower the over potentials and hence enhance the catalytic activity towards the methanol oxidation.

2.2 Electro-catalysts for DMFCs

Platinum and platinum-based electro-catalysts have showed reasonable rate for the electro-oxidation of methanol. Platinum-Nickel oxide/C electro-catalyst has been synthesized for the oxidation of methanol. Four various electro-catalysts have been prepared such as Pt/C, Pt-NiO/C-1, Pt-NiO/C-2 and Pt-NiO/C-3. Pt-NiO/C-3 was prepared from the already formed Pt-NiO/C-1 powder is further subjected for heating at 400°C for 3 hrs in air. The results obtained from the cyclic voltammetry has shown that Pt-NiO/C-3 has higher current density of about 49.22 mA/cm^2 as compare to the Pt/C, Pt-NiO/C-1 and Pt-NiO/C-2 having current densities of about 10.24, 13.46 and 41.10 mA/cm^2. Higher electro-catalytic activity was observed for Pt-NiO/C-3 [3].

Platinum decorated PdCu/C electro-catalyst for oxidation of methanol has been successfully synthesized. Two electro-catalysts have been prepared and compared with each other such as Pt/C and Platinum-PdCu/C. The electrochemical properties show that Pt-PdCu/C has higher current density of about 0.0161 as compare to the 0.0055 A/mgPt for Pt/C. The results indicate that mass activity for Pt-PdCu/C is 4.28 times higher than that of Pt/C for methanol oxidation. It was concluded that Pt-PdCu/C have high stability which makes this a promising candidate for DMFCs applications where it is not economical to use precious metals [4].

PdAu bimetallic alloy nanowires electro-catalyst has been prepared for the oxidation of methanol. During this research, various samples of PdAu has been prepared such as PdAu-0, PdAu-20, PdAu NWs, PdAu-60 and Pd black. The results obtained from the cyclic voltammetry reveals that PdAu NWs has higher electrochemical surface area, that was about 59.10 m^2/g as compare to the 21.43, 31.34, 43.78 and 13.69 m^2/g for PdAu-0, PdAu-20, PdAu-60 and Pd black [5].

2.3 Graphene

Graphene is a two dimensional one-atom-thick planer sheet of sp2 bonded carbon atoms [6]. Graphene is considered to be an ideal electrode and strongest material as compare to the other carbon materials, because it has high surface area, high conductivity, high mechanical properties, low manufacturing cost and unique graphitized basal planer structure makes graphene a promising candidate as a catalyst for low temperature fuel cells [7-9]. Graphene can be utilized for various other applications such as filler for composite materials, transparent electrodes, solar cells, light emitting diodes, optoelectronics, sensors and of course graphene is a promising candidate for electrochemical applications [10]. Graphene was experimentally discovered for the first time in 2004 [11]. Graphene can be considered as the mother of all carbon forms [6]. It has been reported that graphene has a theoretical surface area of about 2630 m^2/g [12].

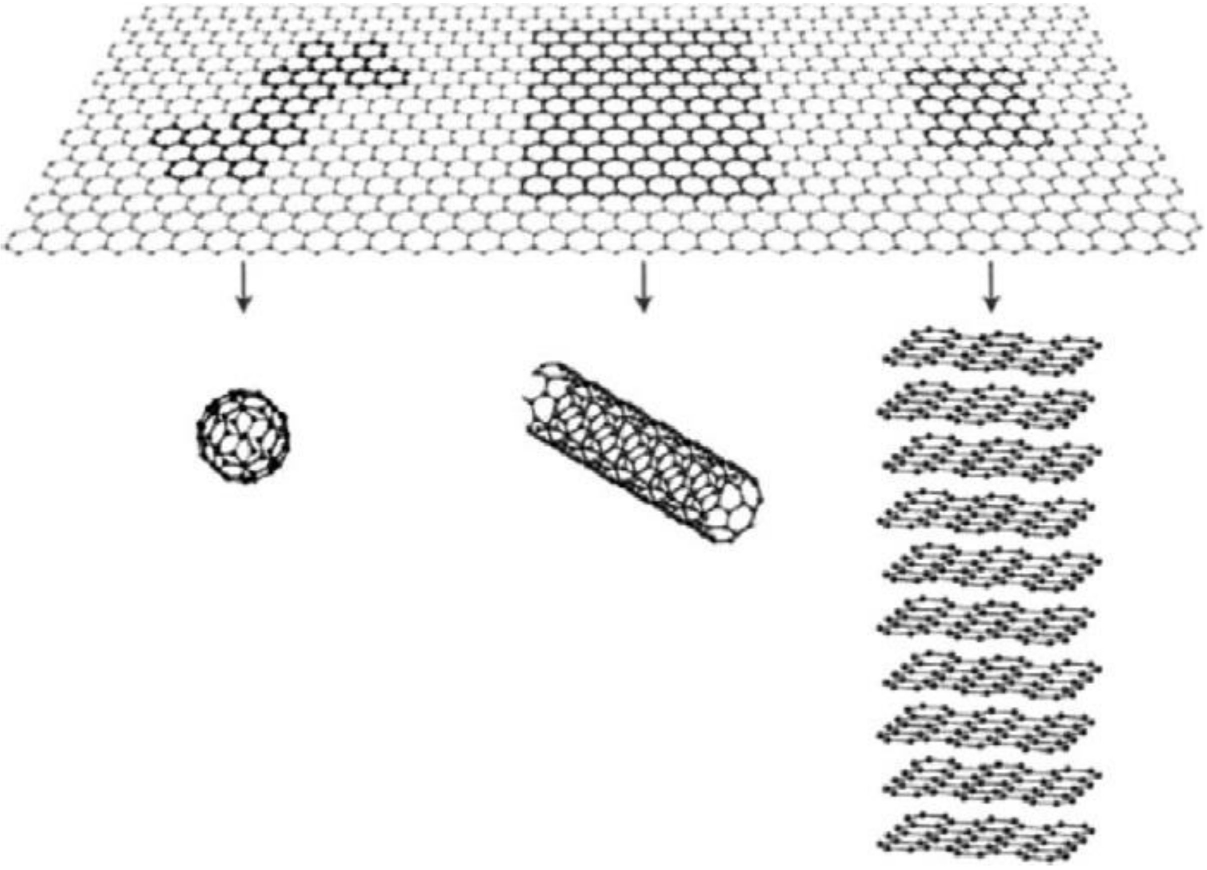


Figure 2.1: Schematic Representation of Graphene [8]

2.4 Graphene based electro-catalysts for DMFCs

Up till now best performing anodic material for electrochemical oxidation of methanol is precious metals like pure platinum or platinum alloys. But due to high cost of such precious metals and low methanol electro-oxidation kinetics caused by these precious metal limits its commercialization. Graphene-platinum composites showed very good performance towards methanol electro-oxidation [13-17]. But at the same time, the catalyst poisoning by carbon monoxide (CO) or CHO species is another big issue for the Pt-based electro-catalysts [18-20]. So, in order to solve such issues non-metals like cobalt (Co), nickel (Ni), lead (Pb) and Tungsten (W) can be utilized to replace platinum and other noble metals in order to reduce the cost of catalyst. Similarly, with the use of high conductive materials as supports such as mesoporous carbon, nanofibers, carbon nanotubes and graphene to improve overall efficiency of DMFCs [21,22]. Other precious metals like gold, silver, copper, palladium, cerium oxide, silicon oxide, titanium dioxide, ruthenium and palladium have also been utilized with graphene to improve electro-catalytic activity and stability. Pt-Graphene nanocomposites have been prepared by a simple way of synthesis which showed very good performance as compare to the Pt-Vulcan. It has been reported that Pt-Graphene had shown peak current density of about 199.6 mA/mg, whereas Pt-Vulcan showed smaller value of current density which was 101.2 mA/mg [23].

Graphene-CeO_2 with support of platinum nanoparticles has been successfully synthesized using the hydrothermal method, where reaction is performed for 4 hours at 160°C into an autoclave. The composite has been observed at various concentrations such as Pt-3% CeO_2/GN, Pt5% CeO_2/GN, Pt-7% CeO_2/GN and Pt-10% CeO_2/GN. The obtained results showed that Pt-7% CeO_2/GN has higher value of forward anodic peak current density which was 440.1 mA/mg as compare to the other composites having current densities 279.5 mA/mg, 324.8 mA/mg and 402.9 mA/mg for Pt-3% CeO_2/GN, Pt-5% CeO_2/GN and Pt-10% CeO_2/GN [24]. Nickel-Copper/Graphene nanoparticle has been successfully synthesized by using hydrothermal method. During the research, electro-catalyst has been observed at various concentrations such as $Ni_{0.25}Cu_{0.75}$, $Ni_{0.6}Cu_{0.4}$ and $Ni_{0.25}Cu_{0.75}$ and 200mg of graphene oxide for each electro-catalyst. The obtained results showed significant methanol oxidation. It has been observed that $Ni_{0.75}Cu_{0.25}$/G has higher value of current density of about 10.35 mA/cm^2 as compare to the $Ni_{0.6}Cu_{0.4}$/G and $Ni_{0.25}Cu_{0.75}$/G having values of current density of about 10.03 mA/cm^2 and 7.44 mA/cm^2. During the research, it was found that as we increase the concentration of methanol, the current density also increases for $Ni_{0.75}Cu_{0.25}$/G electro-catalyst [25]. Palladium/Graphene electro-catalyst has been successfully synthesized by using simple one-pot process. During this research PdNPs/PVP-Graphene, PdNPs/Graphene and PdNPs/Vulcan has been prepared in order to check their response towards methanol oxidation. The obtained results reveal that PdNPs/PVP-Graphene has shown excellent performance towards methanol oxidation as compare to the PdNPs/Graphene and PdNPs/Vulcan [26].

In another research Pd-Ru Nano-particles decorated on graphene Nano sheets has been synthesized by using microwave-assisted polyol reduction method in order to observe the response of prepared electro-catalyst towards methanol oxidation. During the research, several electro-catalysts has been prepared and compared with each other such as 40%Pd/MWCNT, 40%Pd/GNS, 40%Pd-1%Ru/GNS, 40%Pd-3%Ru/GNS, 40%Pd-5%Ru/GNS, 40%Pd-6%Ru/GNS and 40%Pd-10%Ru/GNS. The electrochemical properties show that 40%Pd-5%Ru/GNS has higher value of current density of about 71 mA/cm^2 as compare to the other synthesized electro-catalysts has values of current densities 16mA/cm^2, 27mA/cm^2, 38mA/cm^2, 41mA/cm^2, 43mA/cm^2 and 26mA/cm^2 for 40%Pd/MWCNT, 40%Pd/GNS, 40%Pd-1%Ru/GNS, 40%Pd-3%Ru/GNS, 40%Pd-6%Ru/GNS and 40%Pd-10%Ru/GNS [27]. Platinum-Cobalt nanoparticles decorated on expanded graphite has been synthesized by using solution-phase reduction method and ethylene glycol as a solvent. In this research three electro-catalyst has been compared such as Pt/C, PtCo/MWCNT and PtCo/EG for methanol oxidation. The results obtained during the research has shown that PtCo/EG has higher value of forward current that was about 525.08 mA/mg as compare to the other two electro-catalysts having values of forward currents of about 320.75 mA/mg and 474.59 mA/mg for Pt/C and PtCo/MWCNT [28].

Iron-Platinum nano alloys decorated on graphene has been successfully prepared for the oxidation of methanol. In this research two electro-catalyst has been prepared for the comparison such as Pt/RGO and FePt/RGO. The obtained results reveal that FePt/RGO has higher value of steady current density of about 8.9 mA/mg as compare to the Pt/RGO having steady current density value of about 3.5 mA/mg. So, it has been concluded that FePt/RGO electro-catalyst has higher electro-catalytic activity and stability, and can be considered as a promising candidate for methanol oxidation [29].

Simultaneous Platinum (Pt) deposition and Nitrogen (N) doping of graphene has been synthesized by using hydrothermal method. The electrochemical properties of the prepared electro-catalyst have shown that Pt-NG has higher value of electrochemical surface area (ECSA) of about 78.55 m^2/g as compare to the Pt-G having value of ECSA of about 65.60 m^2/g. It has been concluded that Pt-NG can be considered as a promising candidate for methanol oxidation as it shows higher electro-catalytic activity and stability [30].

Platinum-Nickel nanodendrites decorated on graphene has been successfully synthesized. During the research work Pt/C, PtRu/C, c-PtNi/G, d-PtNi and d-PtNi/G were compared.

The electrochemical properties show that the current density of d-PtNi/G was about 70.9 mA/g which is 12 times higher than the other electro-catalysts such as 22, 0.1, 7.5 and 5.8 mA/g for d-PtNi, c-PtNi/G, PtRu/C and Pt/C. d-PtNi/G has shown very large electrochemical surface area (ECSA) as compare to the others which means that it has higher electro-catalytic activity and stability towards methanol oxidation [31].

Platinum-Silicon dioxide decorated on graphene electro-catalyst has been prepared by using solvothermal synthesis method for methanol oxidation. The prepared electro-catalysts were named as Pt/G, Pt-SiO_2/G-1, Pt-SiO_2/G-2 and Pt-SiO_2/G-3. Pt-SiO_2/G nanocomposites has been prepared with various amounts of tetraethyl orthosilicate (TEOS).

Table 2.1: Pt-SiO2/G nanocomposites with various amounts of TEOS

Samples	TEOS (mg)	SiO_2 content (wt %)	Pt content (wt %)
Pt/G	0	0	20.28
Pt-SiO_2/G-1	11.2	5.78	22.96
Pt-SiO_2/G-2	18.6	9.24	25.16
Pt-SiO_2/G-3	31	10.40	21.51

The obtained results from the electrochemical studies has shown that Pt-SiO_2/G-2 has higher value of electrochemical surface area (ECSA) of about 87.19 m^2/g as compare to the Pt/G, Pt-SiO_2/G-1 and Pt-SiO_2/G-3 having electrochemical surface area of about 41.29, 62.53 and 51.30 m^2/g. Hence Pt-SiO_2/G-2 has shown higher electro-catalytic activity and stability towards methanol oxidation. The stability of this catalyst for methanol oxidation increased by approximately 1.64 times, while electro-catalytic activity of this catalyst for methanol oxidation also increased by about 4.2 times [32].

Graphene-wrapped titanium dioxide nanofibers as efficient platinum electro-catalyst for oxidation of methanol has been successfully synthesized using hydrothermal method. Three different electro-catalysts have been prepared during the research in order to observe their response towards methanol oxidation such as Platinum/TiO_2, Platinum/rGO and Platinum/h-rGO@TiO_2-rGO. The electrochemical properties show that Platinum/h-rGO@TiO_2-rGO has higher current density of forward peak such as 324 mA/mg as compare to the 147 and 202 mA/mg for Platinum/TiO_2 and Platinum/rGO. Hence it is concluded that Platinum/h-rGO@TiO_2-rGO shows higher electro-catalytic activity towards methanol oxidation. And it can have considered as a promising electro-catalysts support material for catalytic applications such as direct methanol fuel cells [33].

Nickel-Graphene nanoparticles has been synthesized by using simple solution synthesis method for methanol electrooxidation in alkaline medium. In this paper, Ni/rGo, Ni/G-300ºC, Ni/G-500ºC and Ni/G-700ºC has been reported for methanol electrooxidation. Prepared electro-catalysts have been tested using cyclic voltammetry in 0.1 M NaOH at a scan rate of 100 mV/s. It is concluded that catalyst presents catalytic activity for methanol electrooxidation with peak potential 557, 536 and 573 mV for Ni/G-300, Ni/G-500 and Ni/G-700. Among three electro-catalysts Ni/G-500 has showed highest peak current density of 20 mA/cm^2 [34].

Graphene-cobalt hydroxide has been prepared for oxygen reduction reaction in alkaline media. Graphene-cobalt hydroxide has been tested by using cyclic voltammetry in 0.1 M KOH. It has been concluded that graphene-Co $(OH)_2$ exhibits excellent catalytic activity for reduction of oxygen to OH^- in 0.1 M KOH. At graphene modified glassy carbon electrode oxygen reduction undergoes two successive 2-electrons processes with HO_2^- as intermediate. However, after electrochemical treatment in 10 mM Co $(NO_3)_2$, not only precipitation of Co $(OH)_2$ but also activation graphene occurs. The activated graphene helps in decreasing overpotential. Combination of graphene with Co $(OH)_2$ results in 4-electron oxygen reduction at lower overpotential [35].

Co_x-Ni_y-decorated graphene has been prepared by using hydrothermal method for methanol oxidation. Ni-Gr, Co-Gr, $Co_{0.2}Ni_{0.2}$-Gr and $Co_{0.3}Ni_{0.1}$-Gr has been tested by using cyclic voltammetry at a scan rate of 50 mV/s at various concentration of methanol.

Table 2.2: Charge Transfer Resistance for utilized electrodes at various concentration of methanol

Electrode	Methanol Concentration			
	0.0	1.0	2.0	3.0
Co-Gr	-	-	6.601	5.128
Ni-Gr	-	-	14.595	5.788
$Co_{0.2}Ni_{0.2}$	-	12.0932	3.168	2.824

It has been concluded that high electro-catalytic activity and good chemical corrosion resistance can be obtained from Co-Ni decorated graphene. Calcination of the resulted decorated graphene in argon atmosphere is an important step to produce solid of Co-Ni alloy nanoparticle. Due to the excellent adsorption capacity and high electrical conductivity, utilizing graphene as a supporter material enhances the electro-catalytic activity towards methanol. $Co_{0.2}Ni_{0.2}$ reveals the best results among the prepared electro-catalysts [36].

Summary

Electro-catalysts take part in an electrochemical reaction. Basically, electro-catalysts work at the electrode surface. Both electrodes (Anode and Cathode) are suffering from large over potentials. However various electrode materials have been reported to lower the over potential and hence enhance the catalytic activity towards the methanol oxidation. Platinum and Platinum based electro-catalysts have showed significant electrooxidation of methanol. Various electro-catalysts have been reported in literature such as Pt/C, Pt-NiO/C, Pt decorated PdCu/C, PdAu bimetallic alloy nanowires electro-catalysts has been reported in literature. Graphene is an ideal candidate as an electrode material as compare to the other carbon materials due to its high conductivity, high mechanical properties, unique graphitized basal planer structure and low manufacturing cost. Graphene based electro-catalysts for direct methanol fuel cells have been reported such as Pt/Graphene, Graphene-CeO_2, Ni-Cu/Graphene, Palladium/Graphene, Pd-Ru nanoparticles decorated on graphene, PtCo/MWCNT, PtCo/EG, Pt/RGO, FePt/RGO, Pt-NG, Pt-SiO_2/G, Ni/Graphene and Co-Ni decorated graphene for the oxidation of methanol.

References

[1] Zainoodin, A. M., Siti Kartom Kamarudin, and Wan Ramli Wan Daud. "Electrode in direct methanol fuel cells." International Journal of Hydrogen Energy 35.10 (2010): 4606-4621.

[2] Hoogers, Gregor, ed. Fuel cell technology handbook. CRC press, 2002.

[3] Amin, R. S., et al. "Pt–NiO/C anode electrocatalysts for direct methanol fuel cells." Electrochimica Acta 59 (2012): 499-508.

[4] Wang, Rongfang, et al. "Pt decorating PdCu/C as highly effective electrocatalysts for methanol oxidation." Electrochemistry Communications 11.5 (2009): 1089-1091.

[5] Wang, Qiao-Li, et al. "Bimetallic PdAu alloyed nanowires: Rapid synthesis via oriented attachment growth and their high electrocatalytic activity for methanol oxidation reaction." Journal of Alloys and Compounds 684 (2016): 379-388.

[6] Brownson, Dale AC, Dimitrios K. Kampouris, and Craig E. Banks. "An overview of graphene in energy production and storage applications." Journal of Power Sources 196.11 (2011): 4873-4885.

[7] Ma, Junhong, et al. "Enhanced electrocatalytic activity of Pt nanoparticles supported on functionalized graphene for methanol oxidation and oxygen reduction." Journal of colloid and interface science 457 (2015): 102-107.

[8] Antolini, Ermete. "Graphene as a new carbon support for low-temperature fuel cell catalysts." Applied Catalysis B: Environmental 123 (2012): 52-68.

[9] Huang, Huajie, et al. "Graphene nanoplate-Pt composite as a high performance electrocatalyst for direct methanol fuel cells." Journal of Power Sources 204 (2012): 46-52.

[10] Choi, Hyun-Jung, et al. "Graphene for energy conversion and storage in fuel cells and supercapacitors." Nano Energy 1.4 (2012): 534-551.

[11] Novoselov, Kostya S., et al. "Electric field effect in atomically thin carbon films." science 306.5696 (2004): 666-669.

[12] Pumera, Martin. "Electrochemistry of graphene: new horizons for sensing and energy storage." The Chemical Record 9.4 (2009): 211-223.

[13] Yoo, EunJoo, et al. "Enhanced electrocatalytic activity of Pt subnanoclusters on graphene nanosheet surface." Nano letters 9.6 (2009): 2255-2259.

[14] Zhou, Yi-Ge, et al. "A facile approach to the synthesis of highly electroactive Pt nanoparticles on graphene as an anode catalyst for direct methanol fuel cells." Chemical Communications 46.32 (2010): 5951-5953.

[15] Li, Yongjie, et al. "Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation." Carbon 48.4 (2010): 1124-1130.

[16] Awasthi, R., and R. N. Singh. "Graphene-supported Pd–Ru nanoparticles with superior methanol electrooxidation activity." Carbon 51 (2013): 282-289.

[17] Choi, Sung Mook, et al. "Synthesis of surface-functionalized graphene nanosheets with high Pt-loadings and their applications to methanol electrooxidation." Carbon 49.3 (2011): 904-909.

[18] Shen, Jianfeng, et al. "Pt–Co supported on single-walled carbon nanotubes as an anode catalyst for direct methanol fuel cells." Electrochimica Acta53.24 (2008): 7276-7280.

[19] Yen, Clive H., et al. "Chemical fluid deposition of Pt-based bimetallic nanoparticles on multiwalled carbon nanotubes for direct methanol fuel cell application." Energy & fuels 21.4 (2007): 2268-2271.

[20] Frackowiak, Elzbieta, et al. "Carbon nanotubes with Pt–Ru catalyst for methanol fuel cell." Electrochemistry Communications 8.1 (2006): 129-132.

[21] Zhao, Xinsheng, et al. "Multi-wall carbon nanotube supported Pt–Sn nanoparticles as an anode catalyst for the direct ethanol fuel cell." Carbon42.15 (2004): 3263-3265.

[22] Yoo, EunJoo, et al. "Enhanced electrocatalytic activity of Pt subnanoclusters on graphene nanosheet surface." Nano letters 9.6 (2009): 2255-2259.

[23] Li, Yueming, Longhua Tang, and Jinghong Li. "Preparation and electrochemical performance for methanol oxidation of Pt/graphene nanocomposites." Electrochemistry Communications 11.4 (2009): 846-849.

[24] Yu, Shuping, et al. "Graphene–CeO 2 hybrid support for Pt nanoparticles as potential electrocatalyst for direct methanol fuel cells." Electrochimica Acta94 (2013): 245-251.

[25] Motlak, Moaaed, et al. "NiCu bimetallic nanoparticle-decorated graphene as novel and cost-effective counter electrode for dye-sensitized solar cells and electrocatalyst for methanol oxidation." Applied Catalysis A: General 501 (2015): 41-47.

[26] Zhang, Yuting, et al. "Facile synthesis of palladium–graphene nanocomposites and their catalysis for electro-oxidation of methanol and ethanol." Electrochimica Acta 109 (2013): 570-576.

[27] Awasthi, R., and R. N. Singh. "Graphene-supported Pd–Ru nanoparticles with superior methanol electrooxidation activity." Carbon 51 (2013): 282-289.

[28] Chen, Maojun, et al. "PtCo nanoparticles supported on expanded graphite as electrocatalyst for direct methanol fuel cell." Electrochimica Acta 165 (2015): 105-109.

[29] Guo, Jinxue, et al. "FePt nanoalloys anchored reduced graphene oxide as high-performance electrocatalysts for formic acid and methanol oxidation." Journal of Alloys and Compounds 604 (2014): 286-291.

[30] Tao, Li, et al. "Simultaneous Pt deposition and nitrogen doping of graphene as efficient and durable electrocatalysts for methanol oxidation." International Journal of Hydrogen Energy 40.41 (2015): 14371-14377.

[31] Luo, Baomin, et al. "Synthesis and electrochemical properties of graphene supported PtNi nanodendrites." Electrochemistry Communications 23 (2012): 72-75.

[32] Vu, Thu Ha Thi, et al. "Solvothermal synthesis of Pt-SiO2/graphene nanocomposites as efficient electrocatalyst for methanol oxidation."Electrochimica Acta 161 (2015): 335-342.

[33] Zhuang, Wei, et al. "TiO 2 nanofibers heterogeneously wrapped with reduced graphene oxide as efficient Pt electrocatalyst supports for methanol oxidation." International Journal of Hydrogen Energy 40.9 (2015): 3679-3688.

[34] Zhang, Ling-Rong, et al. "Preparation of graphene supported nickel nanoparticles and their application to methanol electrooxidation in alkaline medium." New Journal of Chemistry 36.4 (2012): 1108-1113.

[35] Wu, Jiajia, et al. "Catalytic activity of graphene–cobalt hydroxide composite for oxygen reduction reaction in alkaline media." Journal of Power Sources 198 (2012): 122-126.

[36] Barakat, Nasser AM, and Moaaed Motlak. "Co x Ni y-decorated graphene as novel, stable and super effective non-precious electro-catalyst for methanol oxidation." Applied Catalysis B: Environmental 154 (2014): 221-231.

Chapter 3

Review on Characterization and Experimentation Methods

3.1 Cyclic Voltammetry

Cyclic voltammetry is the most commonly used technique to obtain qualitative information about electrochemical reactions. CV can also be used to get kinetic information of electrode reactions, where electrode reaction usually involves electron-transfer reaction which is influenced by electrode potential. Basically, in cyclic voltammetry technique, the working electrode potential is ramped linearly versus time. In cyclic voltammetry, after reaching to the set potential during the experiment, the working electrode's potential is encouraged to ramped in backward (opposite) direction in order to reach its initial position. Cyclic voltammogram trace is obtained, while plotting current at the working electrode versus the applied voltage as shown in the figure 3.1.

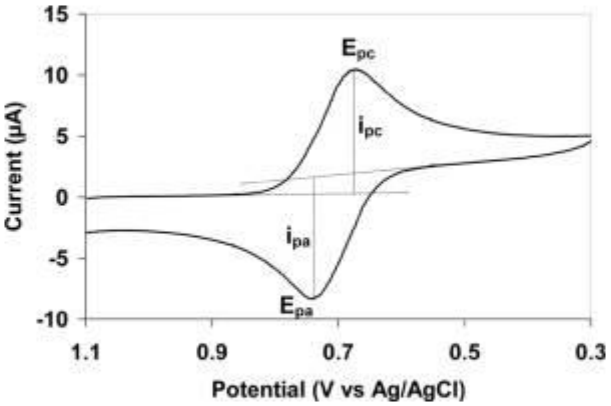


Figure 3.1: Schematic representation of Peak Cathodic and anodic current respectively for a reversible reaction.

The main purpose of cyclic voltammetry is to study the electrochemical properties of an analyte in solution. In a cyclic voltammetry experiment, there is an electrochemical cell containing three electrodes such as Reference electrode, counter electrode and working electrode. In an electrochemical cell these three electrodes are put together in an electrolyte solution that usually contain an electroactive species as shown in the figure 3.2.

Working electrode is the electrode in cyclic voltammetry experiment, where reaction of our interest occurs. Gold, silver, platinum, and glassy carbon are usually considered as working electrode materials. There are some other special types of working electrodes such as rotating ring-disk electrode, rotating disk electrode, dropping mercury electrode and ultramicroelectrode. Reference electrode is the electrode which has a stable electrode potential. There are various types of reference electrodes such as saturated calomel electrode, copper-copper (II) sulfate electrode, silver chloride electrode and silver-silver chloride electrode. Counter electrode is the electrode in an electrochemical system where flow of electric current is expected. Platinum, gold and carbon are the commonly used materials for counter electrode.

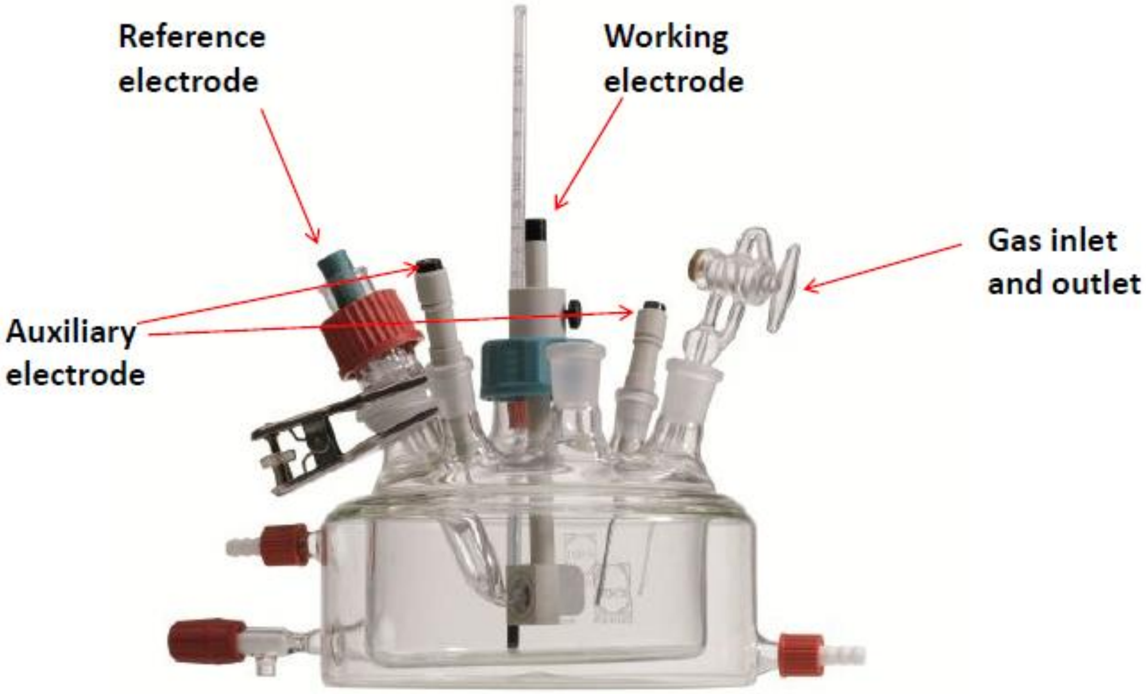


Figure 3.2: Three Electrodes Setup of Cyclic Voltammetry

In cyclic voltammetry potential is usually applied between the reference electrode and working electrode, whereas current is observed between the counter electrode and working electrode. Electrolyte is usually added in order to provide sufficient conductivity. In cyclic voltammetry solvent, electrolyte and working material determines the range of potential that can be observed during experiment.

Cyclic voltammetry has been widely used as an electroanalytical technique in various fields of chemistry. Cyclic voltammetry is used to determine electron transfer kinetics, various redox processes, reversibility of the reaction and electron stoichiometry of a system. It can also be used to determine diffusion coefficient of an analyte and as an identification tool. Concentration of solution which is unknown can also be determined through cyclic voltammetry [1].

3.2 Scanning Electron Microscopy

SEM (Scanning electron microscopy) is a microscope that basically uses electron instead of light in order to form an image. Scanning Electron Microscopy was developed in early 1950's. The main components of Scanning Electron Microscopy are scanning system, detectors, electron column, vacuum system, display and electronics control as shown in figure 3.3.

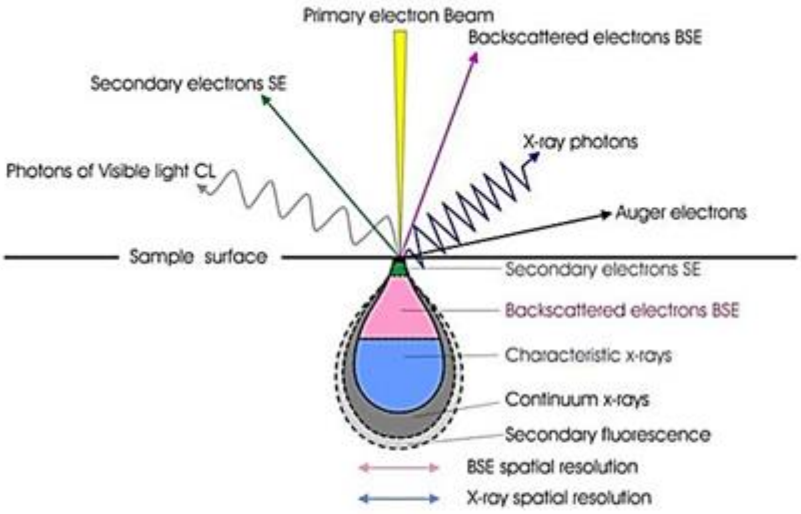


Figure 3.3: Interaction of electron beam with sample surface.

The electron column of Scanning Electron Microscopy (SEM) consists of an electron gun and two or more electromagnetic lenses. The electron gun of the electron column generates electrons and accelerates them to energies in the range from 1 to 40 KeV in the Scanning Electron Microscopy. Whereas the main purpose of electron lenses is to create a small, focused electron probe on the specimen. There are two types of electron gun such as Field emission and thermionic gun. Thermionic is basically a materially that exposes to high temperature so that it emits electrons. While field emission gun, a very strong magnetic field that draws electrons from the metallic tip (Usually Tungsten). In field emission, there are two anodes, where 2KV voltage is applied to create electric field so that electron leaves the tip and second anode is used to accelerate these electrons towards microscope. Combination of these two anodes focuses the beam. Then beam is focused by a condenser lens (Electromagnetic lens) in order to form a probe. After focusing this beam is passed through an aperture which excludes electrons. If there are some inconsistency in the beam that is corrected by stigmators and beam focused onto the sample. Then there are deflector coils that moves the beam back over the sample and signal generated from each area is collected simultaneously to get the final image on the monitor.

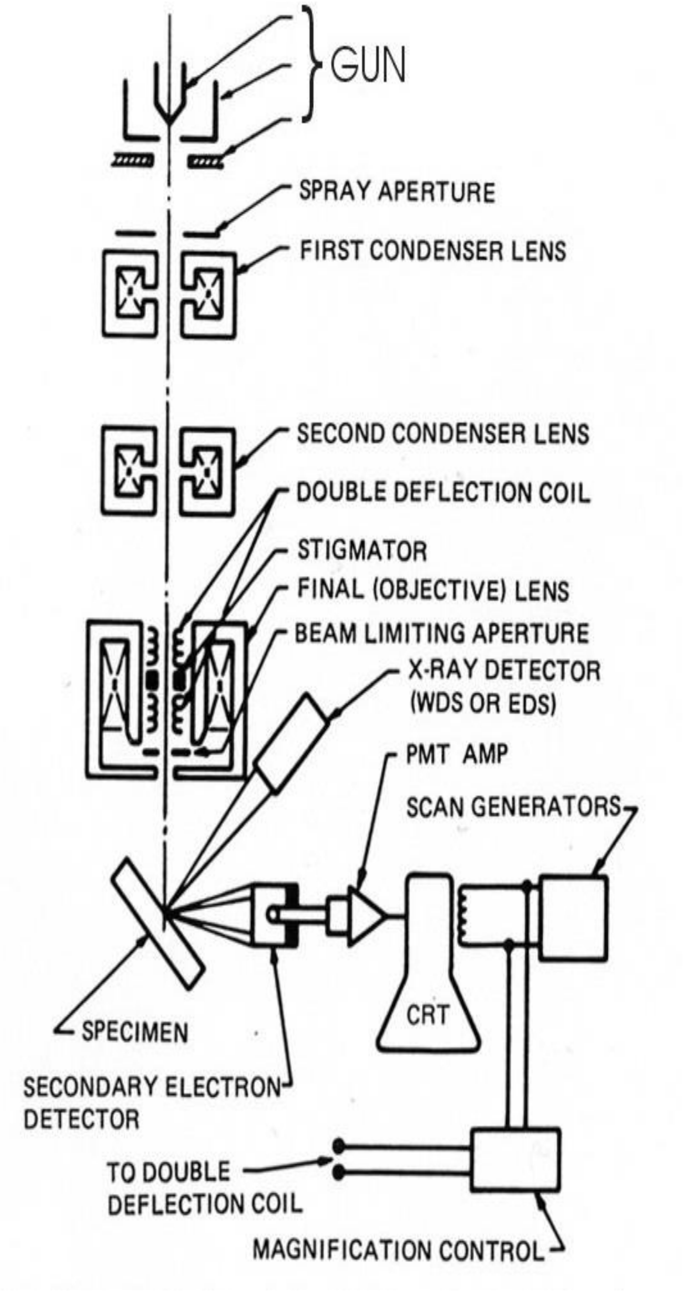


Figure 3.4: Schematic Representation of the drawing of an electron and X-ray optics of a combined SEM-EPMA

The scanning electron microscopy works very fast, it can complete BSE, SEI and EDS analyses in less than five minutes. Scanning electron microscopy is user-friendly and easy to operate with the proper training. Scanning electron microscopy gives us morphological, topographical, and compositional information. It can also detect and analyze fractures, provide qualitative analyses, and identify crystalline structures [2].

3.3 X-ray Diffraction (XRD)

X-ray diffraction is non-destructive technique to characterize the crystalline structure of the prepared electro-catalysts. Lattice parameters, size of crystallites, sample purity, unit cell dimensions and other information related to crystals can be obtained from the XRD. Basically, XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiations (single frequency or wavelength), collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference [3].

When condition satisfy, Bragg's law

$$n\lambda=2d\sin\theta$$

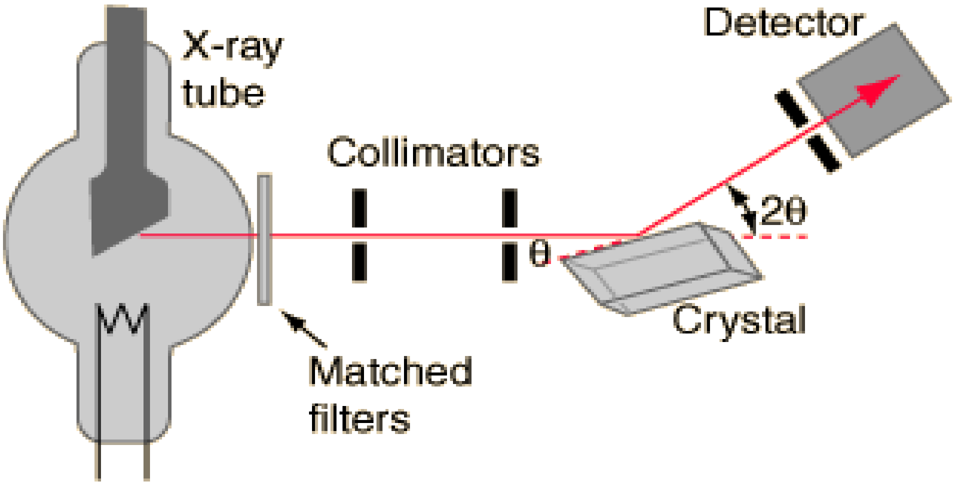


Figure 3.5: Working Principle of XRD

3.4 Experimentation methods

3.4.1 Chemical reduction method

Chemical reduction is the most common method for preparation of nanocomposites. This method involves stirring the mixture of noble metal precursors such as (H_2PdCl_6, K_2PtCl_4 and $HAuCl_4$) and catalyst carrier in order to obtain fully disperse mixture in the first step. In the second step reducing agent is added in the liquid phase. In the final step, the ionic reactants are reduced to metals for the successfully preparation of nanocomposites. Hydrazine hydrate, sodium borohydride and ethylene glycol are usually used as a reducing agent. The chemical reduction method is very simple and easy to operate [4].

Summary

In this chapter a brief review of synthesis of composites have been discussed such as chemical reduction method. Chemical reduction method is the most common method for the preparation of composites. This method is very simple and easy to operate. Various characterization techniques were also discussed in this chapter such as X-ray diffraction to identify phase, structure, crystallite size and lattice parameter whereas scanning electron microscope is used to obtained the information regarding the morphology of sample. X-ray diffraction works on the principle of Bragg’s law whereas in scanning electron microscope a focused electron beam is targeted on the composite, which results in excitation of electrons. Cyclic voltammetry is used to study the electrochemical properties of the prepared electro-catalysts. Cyclic voltammetry is based upon three electrodes setup such as reference electrode, counter electrode and working electrode.

References

[1] https://en.wikipedia.org/wiki/Cyclic_voltammetry

[2] https://en.wikipedia.org/wiki/Scanning_electron_microscope

[3] https://en.wikipedia.org/wiki/X-ray_Diffraction

[4] Wang, Xingxing, et al. "Research Progress of Preparation Methods of Graphene Nanocomposites for Low-Temperature Fuel Cells and Lithium-Ion Batteries." Kemija u Industriji-Journal of chemists and chemical engineers 65.5-6 (2016): 259-264.

Chapter 4

Experimentation

4.1 Synthesis of Graphene Oxide

Graphene oxide has been prepared using improve Hummer's method. In this method graphite powder was used for the preparation of graphene oxide. A beaker with a thermometer containing sulfuric acid (50 ml) was placed in an ice bath. While stirring 0.6 grams of sodium nitrate ($NaNO_3$) is added at a controlled rate into the sulfuric acid (H_2SO_4). After this 1.3 grams of graphite powder is added in order to obtain the expanded graphite.

Till this point the temperature of the reaction mixture should be kept at 20°C. After this 3.8 grams of potassium permanganate were added at a controlled rate. Now the temperature should be increase from 20°C to 30°C and ice bath is removed. Then warm de-ionized water (100 ml) was added drop wise into the solution. It should be confirmed that the temperature should not be fall below 30°C at this point. After this warm hydrogen peroxide (170 ml) was added into the solution in order to obtain dilute dispersion containing graphene oxide with impurities.

To obtain pure graphene oxide, we have used centrifuge and perform various cycles of centrifugation with constant monitoring. During the cleaning of graphene oxide, we have washed solution several times with ethanol (CH_3OH) and distilled water. In the final step the obtained graphene oxide (GO) is placed in a vacuum oven at 50°C for drying [1].

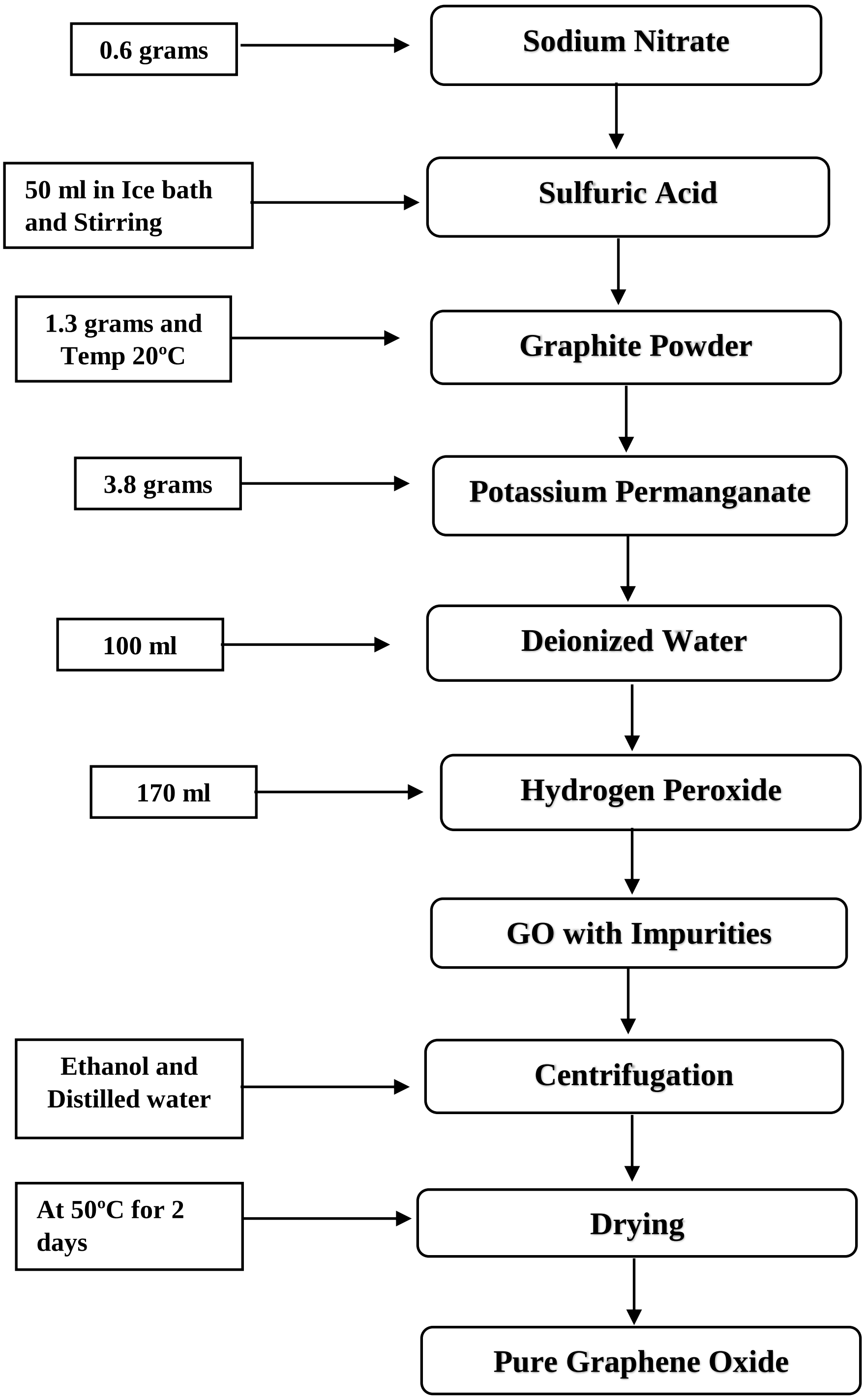


Figure 4.1: Flow Diagram for the preparation of Graphene oxide

4.2 Synthesis of Ni-Co/Graphene composites

Ni-Co/Graphene composite has been prepared using chemical reduction method. In a typical procedure 0.50 mmol of cobalt nitrate hexa-hydrate, 0.50 mmol of nickel sulfate hexa-hydrate (Atomic ratio of Ni:Co=1:1) and 100 mg of graphene oxide were added in 100 ml flask containing 60 ml ethylene glycol as a solvent. After this ultrasonication is performed for one hour in order to well mix the nickel and cobalt particles into the solvent. Then stirring is performed for 24 hours at ambient temperature. Now the ammonia solution is added into the mixture in order to get the pH 10.5. Then 1 ml hydrazine hydrate (N_2H_4) is added as a reducing agent into the mixture. And the reduction reaction is performed at 85°C for 12 hours. We have used the centrifuge for the purification of composite and perform various cycles of centrifugation with constant monitoring. During the cleaning, we have washed our solution several times with distilled water and ethanol. Finally, the obtained product is placed in an vacuum oven at 50°C for drying. Similarly, Ni/Co=2:1 (0.6/0.4 mmol) and Ni/Co 4:1 (0.8/0.2 mmol) with same concentration of graphene oxide (100 mg) were also prepared following the same procedure [2].

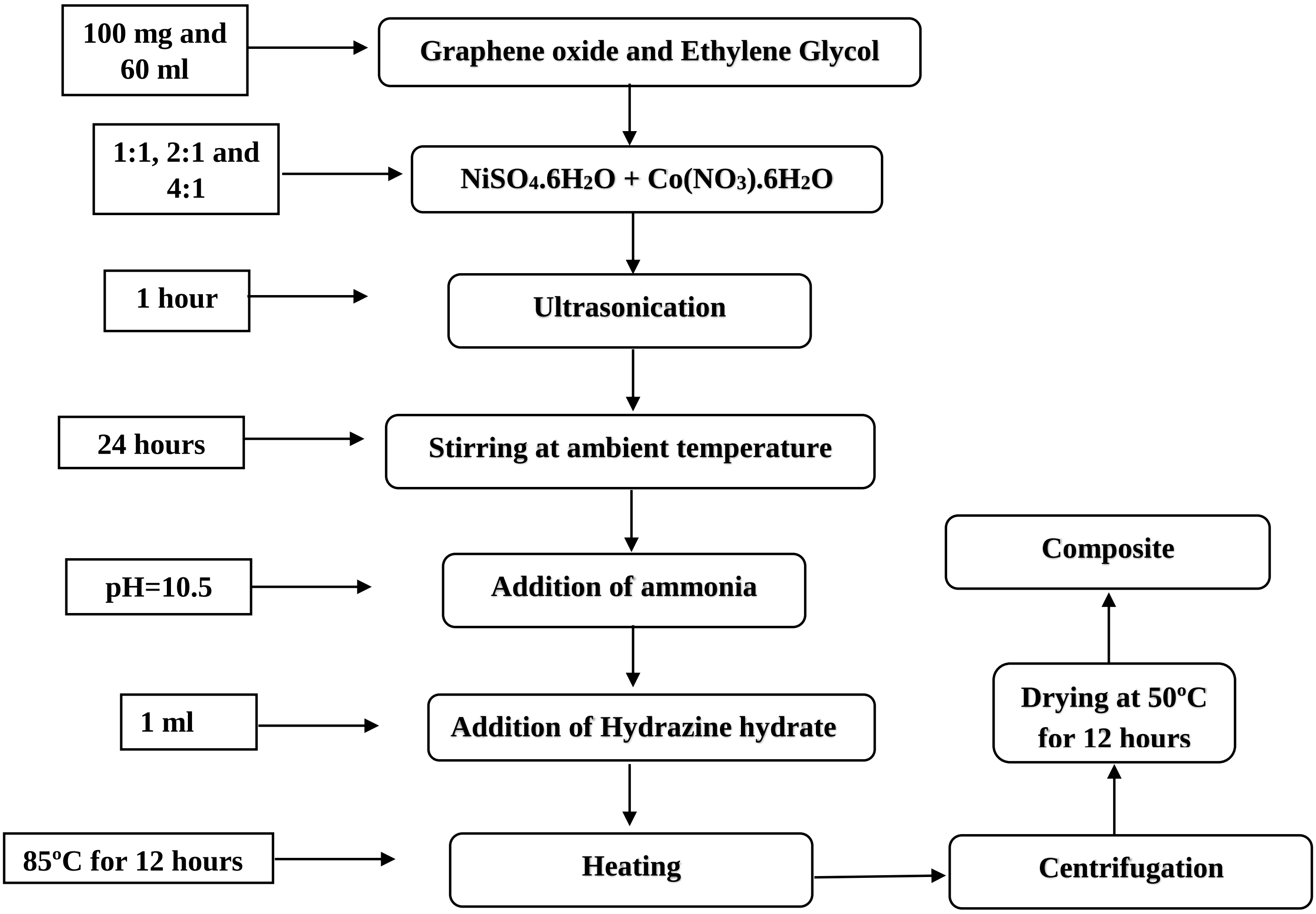


Figure 4.2: Flow diagram for the preparation of Ni-Co/G composites

Figure 4.3: Schematic Diagram of Synthesized Composites

4.3 Preparation of working electrode

For the preparation of working electrode, first of all glassy carbon electrode is polished with alumina slurry. Then GCE was washed with distilled water and dried in open air. After this slurry of 2 mg working material, 20 µl nafion solution and 400 µl of isopropanol is formed. Then 15 µl of the slurry is deposited on the active area of glassy carbon electrode with the help of micro-pipette and dried in open air [3].

Figure 4.4: Working Electrode Preparation

Figure 4.5: GCE and Nafion Solution

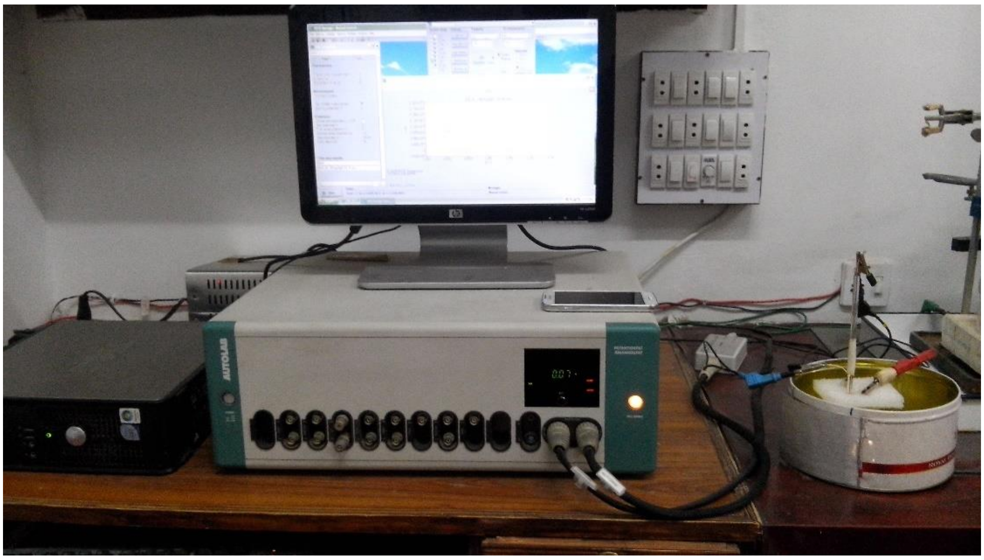


Figure 4.6: Schematic Diagram of AUTOLAB 4.9 potentiostat connected to PC

Figure 4.7: Schematic Diagram of Three Electrodes Setup

Table 4.1: Cyclic Voltammetry Requirements

Working Electrode	**Platinum Electrode (1.5mm)**
Reference electrode	Ag/AgCl
Counter Electrode	Platinum wire
Applied Voltage	-600mV to 200mV
Fuel	3 Molar (Methanol)
Supporting Electrolyte	1 Molar (KOH)
Electrolyte	Nafion Solution

Working Electrode	**Glassy Carbon Electrode (3 mm)**
Reference electrode	Ag/AgCl
Counter Electrode	Platinum wire
Applied Voltage	-200 mV to 1800mV
Fuel	1 Molar (Methanol)
Supporting Electrolyte	1 Molar (KOH)
Electrolyte	Nafion Solution

Summary

In this chapter preparation of graphene based Ni-Co composites has discussed systematically. Initially graphene oxide has been prepared by using improve Hummer’s method. Whereas in the second step graphene based Ni-Co composites has been prepared using simple solution synthesis method. Three electro-catalysts (Ni-Co=1:1, Ni-Co=2:1 and Ni-Co=4:1) have been prepared with different nickel-cobalt ratio to study the effect of Ni-Co ratio on the electrochemical properties of the prepared electro-catalysts. During preparation hydrazine hydrate is used as a reducing agent to convert graphene oxide to graphene. For the preparation of working electrode Nafion solution is used to provide sufficient conductivity, isopropanol is used as a solvent and KOH is used as a supporting electrolyte. For cyclic voltammetry testing, reference electrode is Ag/AgCl, counter electrode is Pt wire and two working electrodes has been used such as Platinum working electrode (1.5 mm) and glassy carbon electrode (3mm).

References

[1] Bong, Sungyool, et al. "Graphene supported electrocatalysts for methanol oxidation." Electrochemistry Communications 12.1 (2010): 129-131.

[2] Hameed, RM Abdel. "Microwave irradiated Ni–MnO x/C as an electrocatalyst for methanol oxidation in KOH solution for fuel cell application." Applied Surface Science 357 (2015): 417-428.

[3] Samant, Purnakala V., and Julio B. Fernandes. "Nickel-modified manganese oxide as an active electrocatalyst for oxidation of methanol in fuel cells." Journal of power sources 79.1 (1999): 114-118.

Chapter 5

Results and Discussion

5.1 Characterization Techniques

5.1.1 X-ray diffraction

The characteristic peak was obtained at 2θ of 11.5° which clearly indicates the formation of graphene oxide (GO) as shown in Fig.5.1. (A). The X-ray diffraction analysis of Ni-Co/graphene shows intensity peaks at 2θ values of 37°, 43° and 62° clearly indicates the formation of nickel oxide or cobalt oxide or both, because nickel and cobalt have same crystal structure, successive atomic numbers, and closer molecular weights under normal conditions as shown in Fig.5.1. (C). In this nanocomposite, there was no any peak indicating the formation of carbon because we have calcined the composite and burning temperature of graphene is 350°C, so that we can say that only little amount of carbon was present in this composite which did not appear in the X-ray diffraction pattern. The other X-ray diffraction analysis of Ni-Co/graphene (B) without calcination shows intensity peaks at 2θ values of 21.69°, 37°, 43° and 62° can be assigned to the characteristic of Face-centered cubic structure, which clearly indicates the formation of pure nickel or pure cobalt or both, because nickel and cobalt have same molecular weights, successive atomic numbers, and same crystal in the normal conditions. On the other side, the X-ray pattern have a sharp peak at 21.69° which indicates the presence of carbon in composite as shown in Fig.5.1. (B).

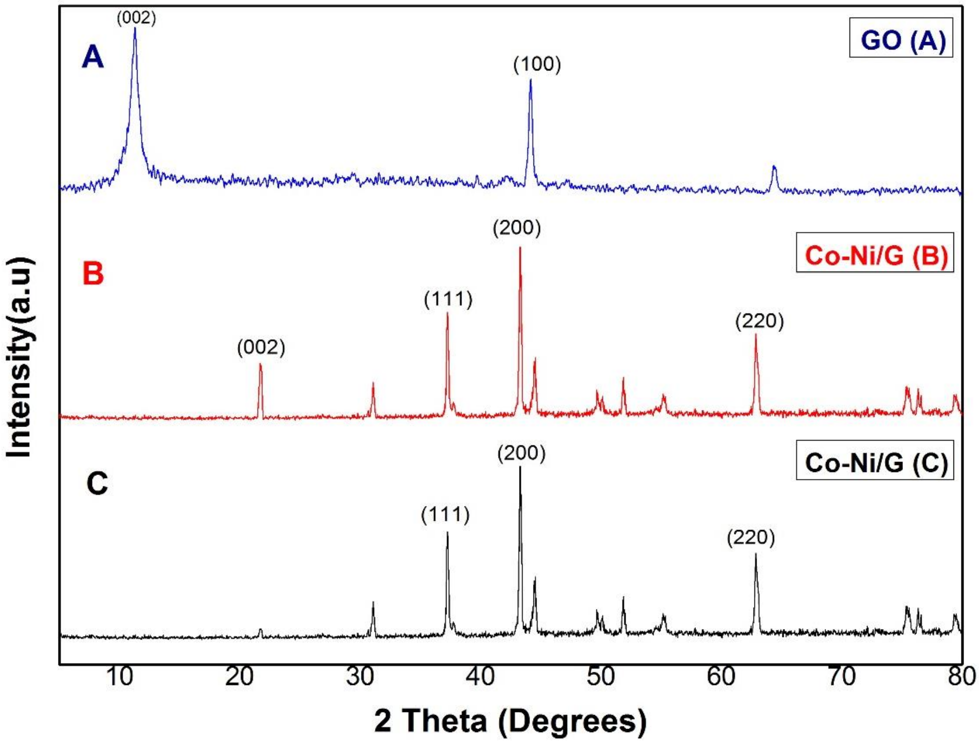


Figure 5.1: XRD Pattern of GO (A), Co-Ni/G (B) and Co-Ni/G (C) with calcination

5.1.2 Scanning Electron Microscope

The SEM images below shows the morphology of the prepared graphene oxide and nanocomposites. In Fig.5.2. (a) wrinkles can be seen which shows the formation of graphene oxide. It can be seen in the Fig.5.2. (b), Fig.5.3. (c) and Fig.5.4. (d) that nickel and cobalt nanoparticles are uniformly dispersed over the sheet of graphene. However, Ni_4-Co_1/G nanocomposite shows that nanoparticles are more uniformly distributed then the Ni_1-Co_1/G and Ni_2-Co_1/G. This may be due to the presence of more concentration of nickel.

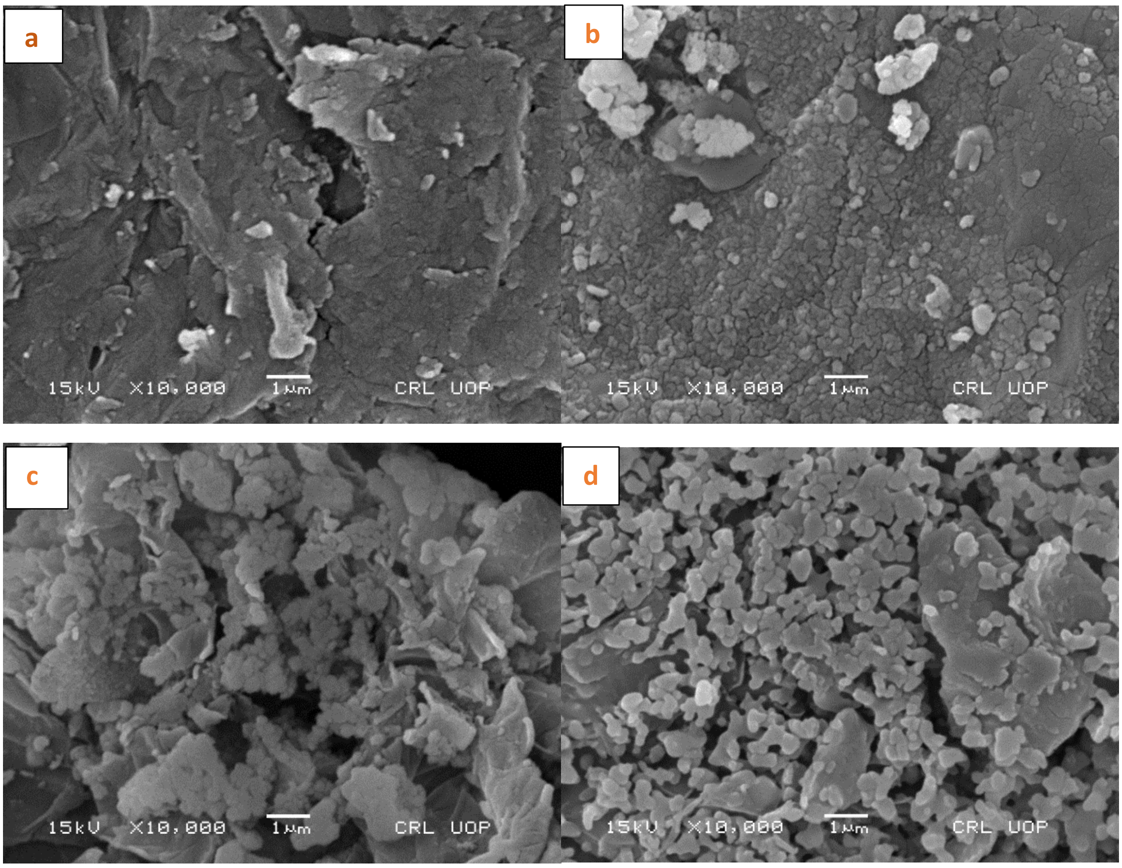


Figure 5.2: SEM image of GO (a), Ni_1-Co_1/G (b), Ni_2-Co_1/G (c) and Ni_4-Co_1/G (d)

5.2 Electrochemical measurements of Ni-Co/graphene nanocomposites

To investigate electro-catalytic activity of Co-Ni/graphene for methanol oxidation, cyclic voltammetry was carried out in 1M KOH containing 3M methanol. The potential -200 mV to 1800 mV for glassy carbon electrode and -600 mV to 200 mV for Pt electrode is applied between the working electrode and the reference electrode while the current is measured against the applied potential.

5.2.1 Modified Platinum Electrode

The current density measured for bare platinum was about 11.5 mA/cm^2 as shown in the Fig. 5.4. And the current density measured for Co_1-Ni_1/G, Co_1-Ni_2/G and Co_1-Ni_4/G was about 19.5, 40.0 and 60.0 mA/cm^2 as shown in the Fig.5.5., Fig.5.6. and Fig.5.7. We observed that as we increase the concentration of nickel in our composite, current density also increases which leads to the formation high electro-catalytic activity towards methanol oxidation. As can be seen from the Fig.5.8., Co_1-Ni_4/G has a better electro-catalytic activity as compare to the other prepared electro-catalysts because of its high current density.

5.2.2 Modified Glassy Carbon Electrode

The current density measured for bare GCE was about 11.6 mA/cm^2 as shown in the Fig.5.10. And the current density measured for Co_1-Ni_1/G, Co_1-Ni_2/G and Co_1-Ni_4/G was about 11.96, 18.0 and 20 mA/cm^2 as shown in the Fig.5.11., Fig.5.12. and Fig.5.13. It was observed that as Ni concentration increases in composite, current density also increases which leads to the high electro-catalytic activity towards methanol oxidation. As can be seen from the Fig.5.14., Co_1-Ni_4/G has a better electro-catalytic activity as compare to the other prepared electro-catalysts because of its high current density.

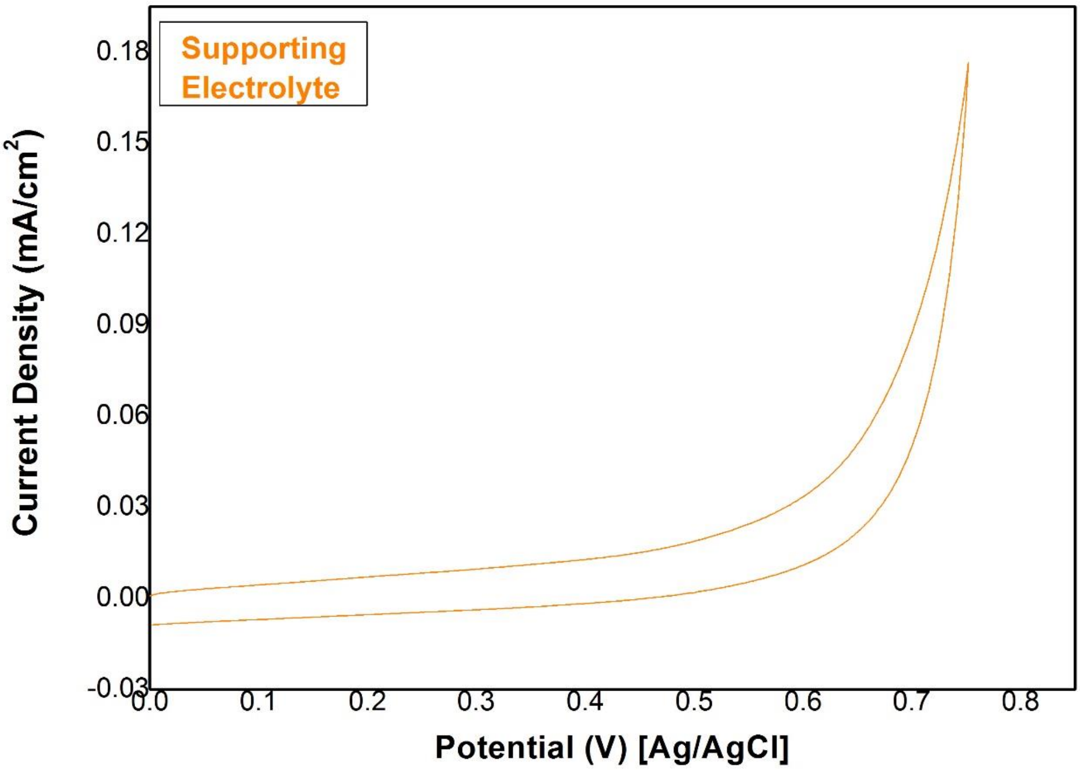


Figure 5.3: Cyclic Voltammogram for Supporting Electrolyte on Pt Electrode

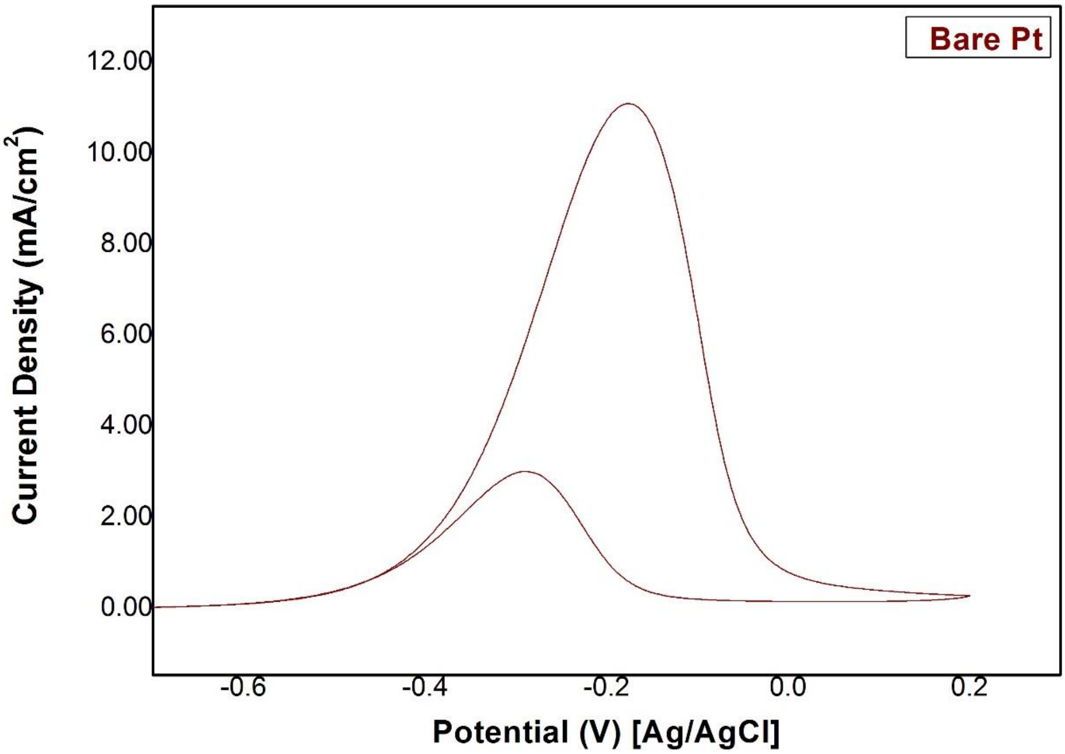


Figure 5.4: Cyclic Voltammogram for Bare Platinum

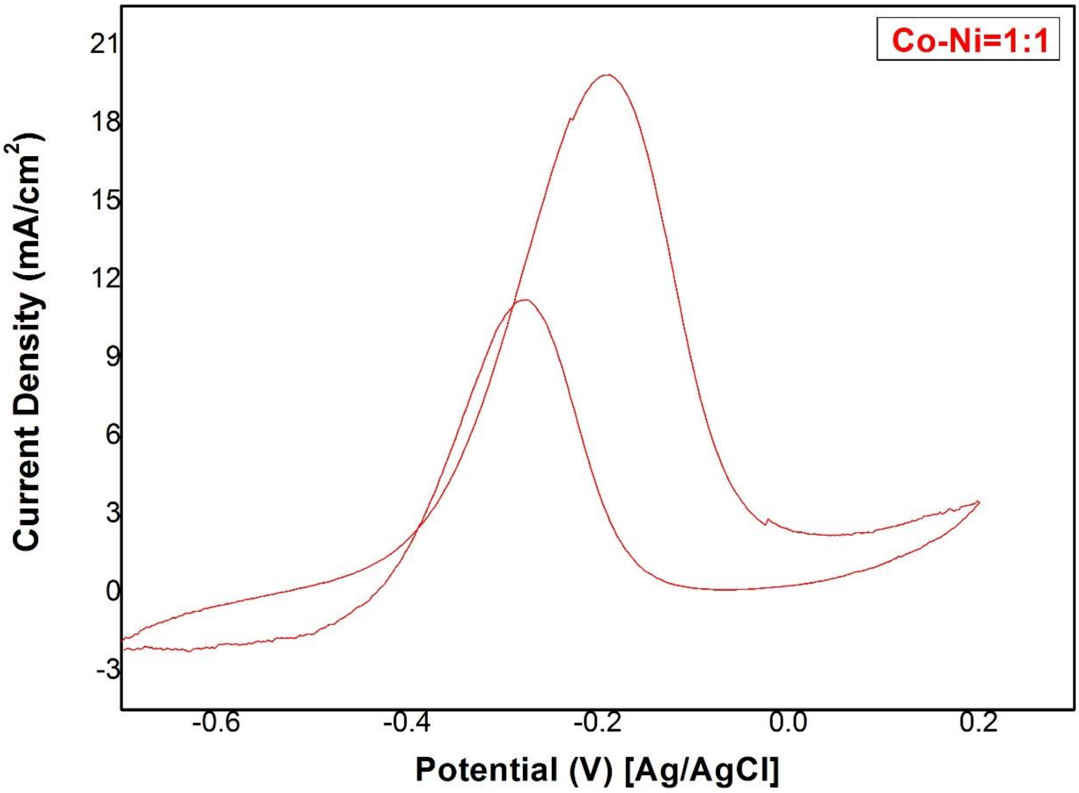


Figure 5.5: Cyclic Voltammogram for Co-Ni=1:1 with graphene on modified Pt Electrode

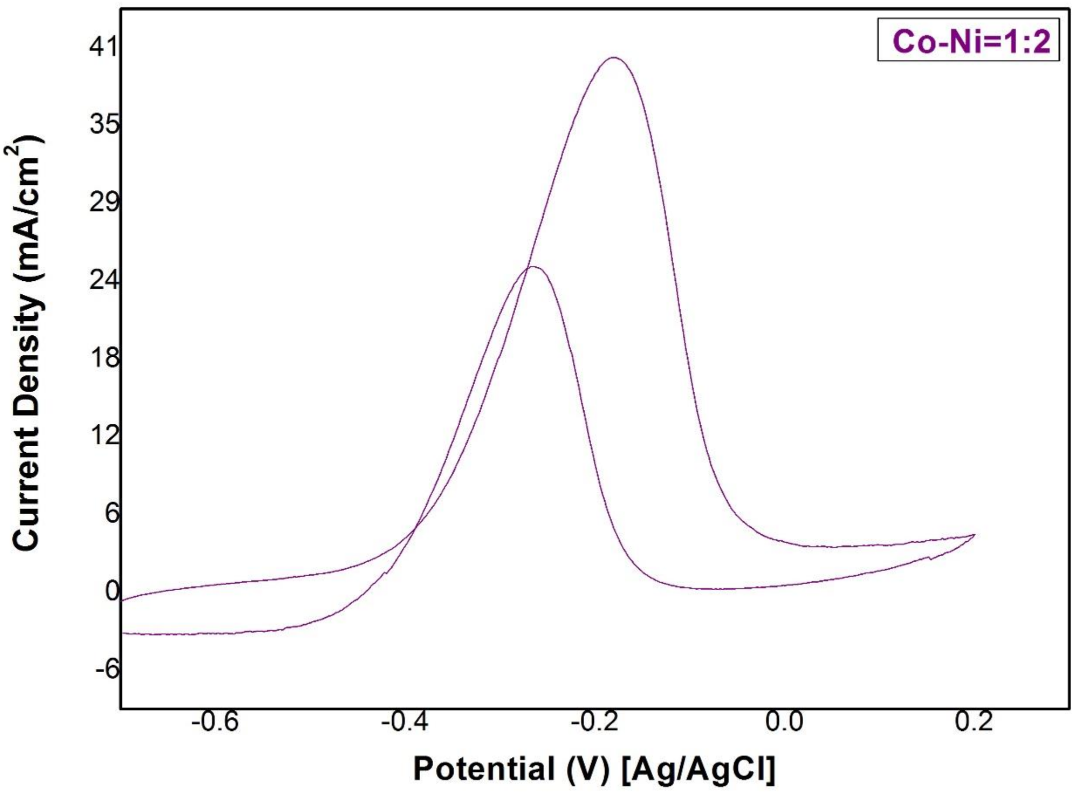


Figure 5.6: Cyclic Voltammogram for Co-Ni=1:2 with graphene on modified Pt Electrode

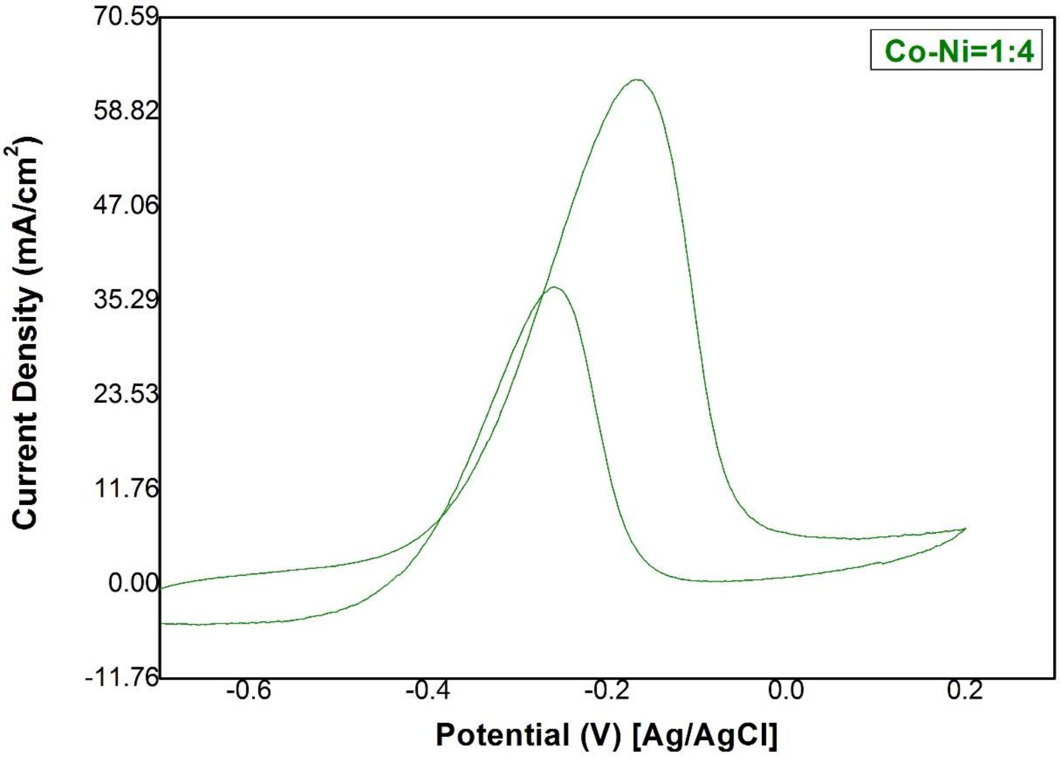


Figure 5.7: Cyclic Voltammogram for Co-Ni=1:4 with graphene on modified Pt Electrode

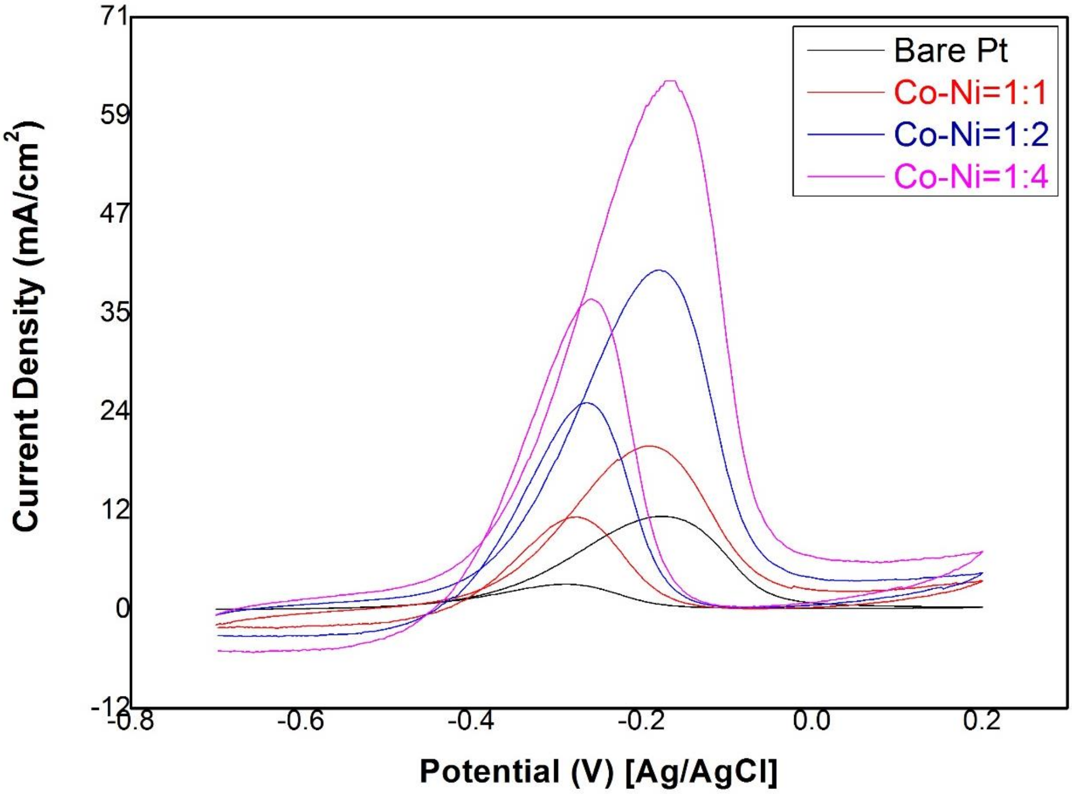


Figure 5.8: Comparison of Various Electro-catalysts on modified Pt Electrode

Table 5.1: Current Densities of Various Electro-catalysts on Pt electrode

Electro-catalysts	**Current Density (mA/cm^2)**
Bare Platinum	11.5
Co-Ni=1:1 with graphene on modified Pt electrode	19.5
Co-Ni=1:2 with graphene on modified Pt electrode	40
Co-Ni=1:4 with graphene on modified Pt electrode	60

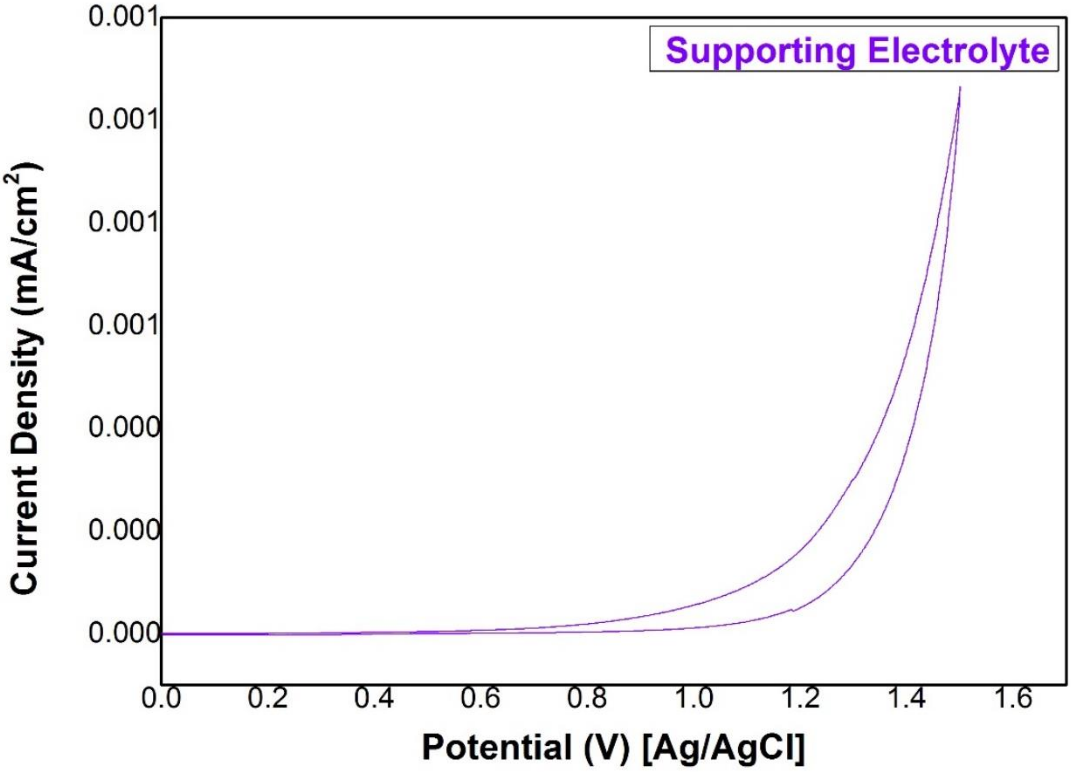


Figure 5.9: Schematic Diagram of Supporting Electrolyte on GCE Electrode

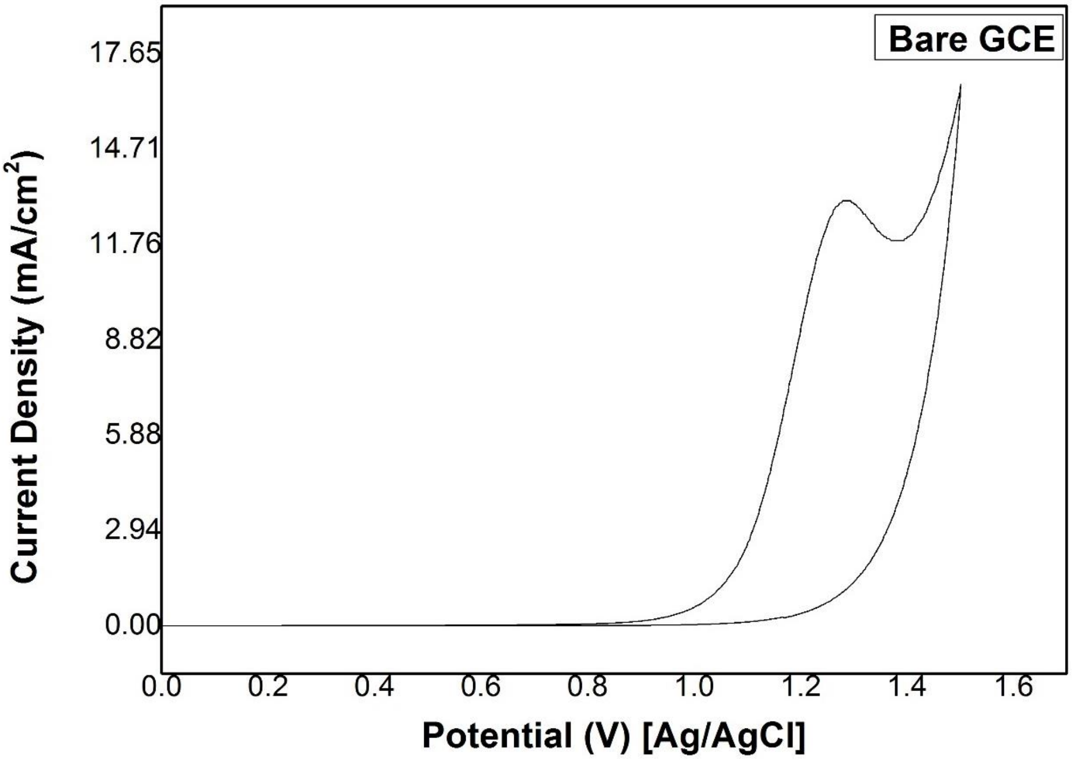


Figure 5.10: Cyclic Voltammogram for Bare GCE

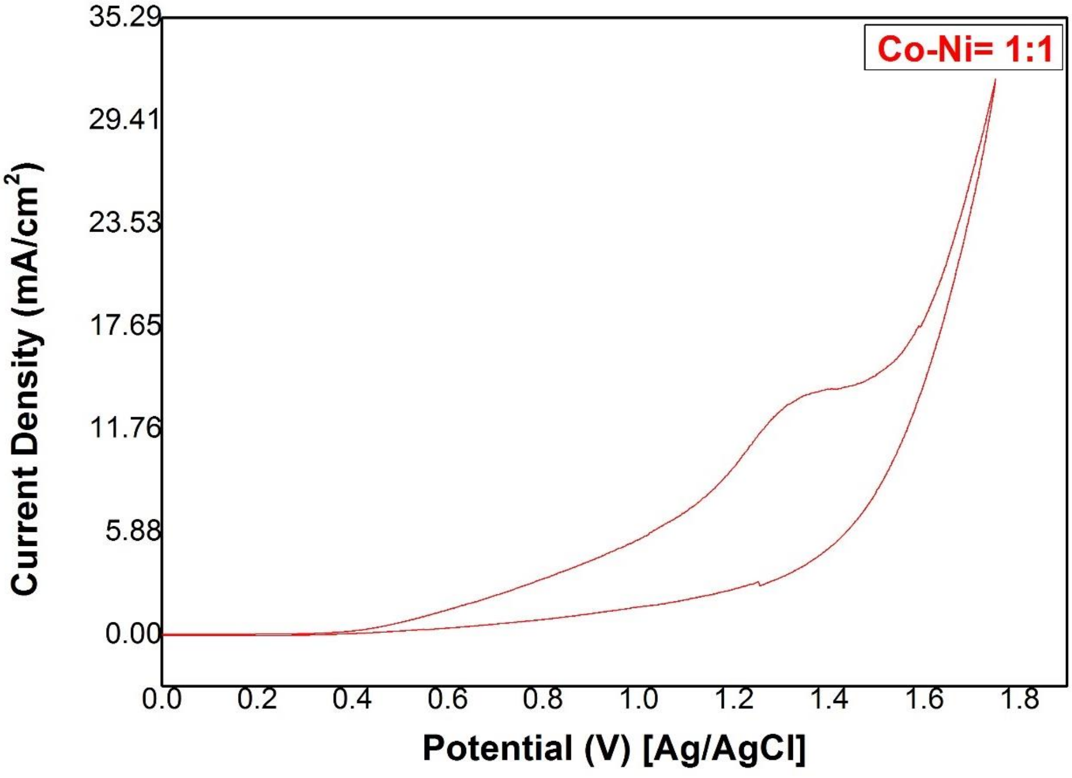


Figure 5.11: Cyclic Voltammogram for Co-Ni=1:1 with graphene on modified GCE

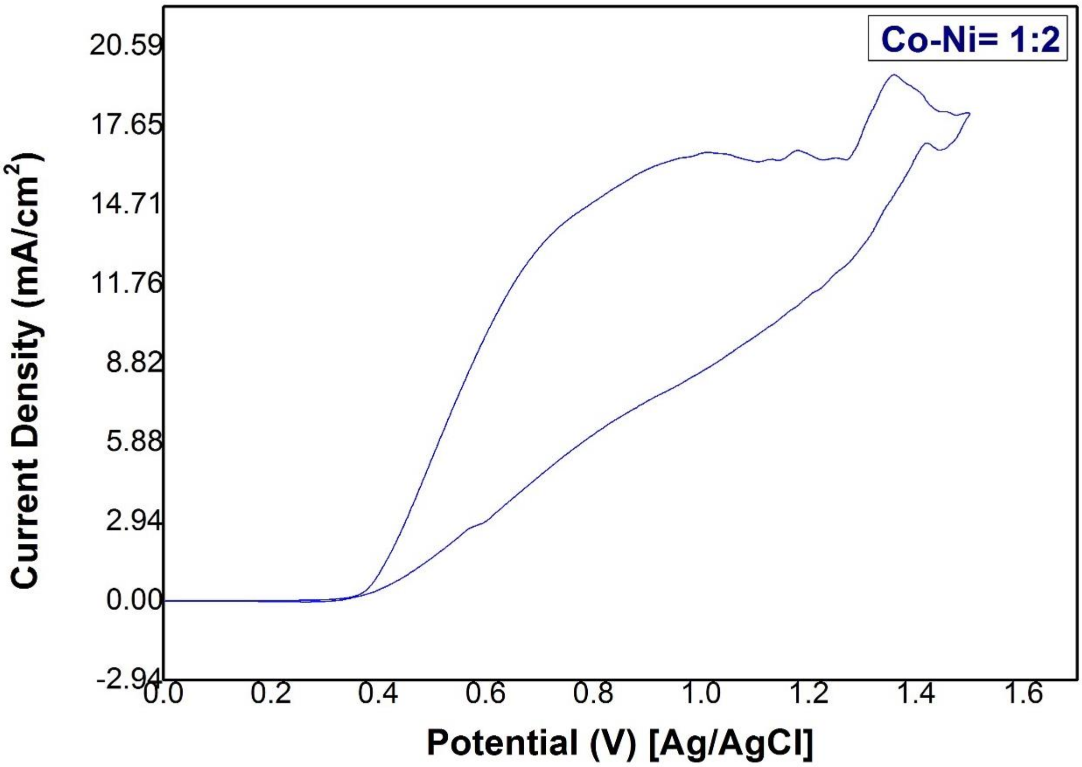


Figure 5.12: Cyclic Voltammogram for Co-Ni=1:2 with graphene on modified GCE

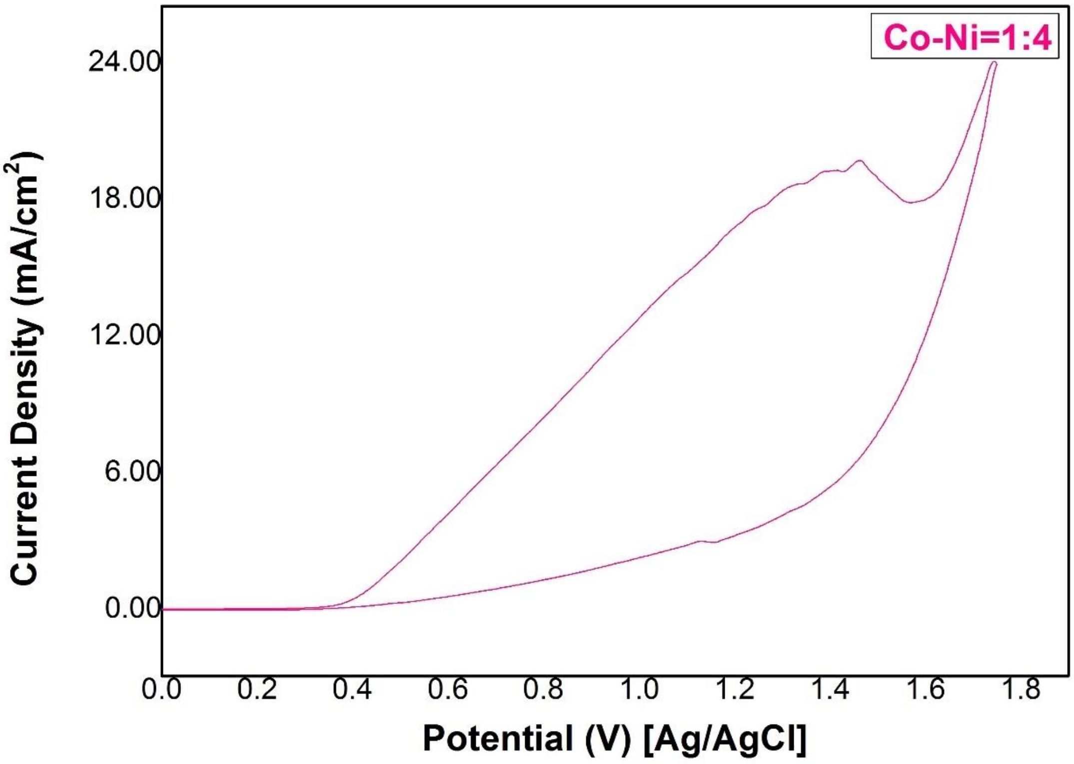


Figure 5.13: Cyclic Voltammogram for Co-Ni=1:4 with graphene on modified GCE

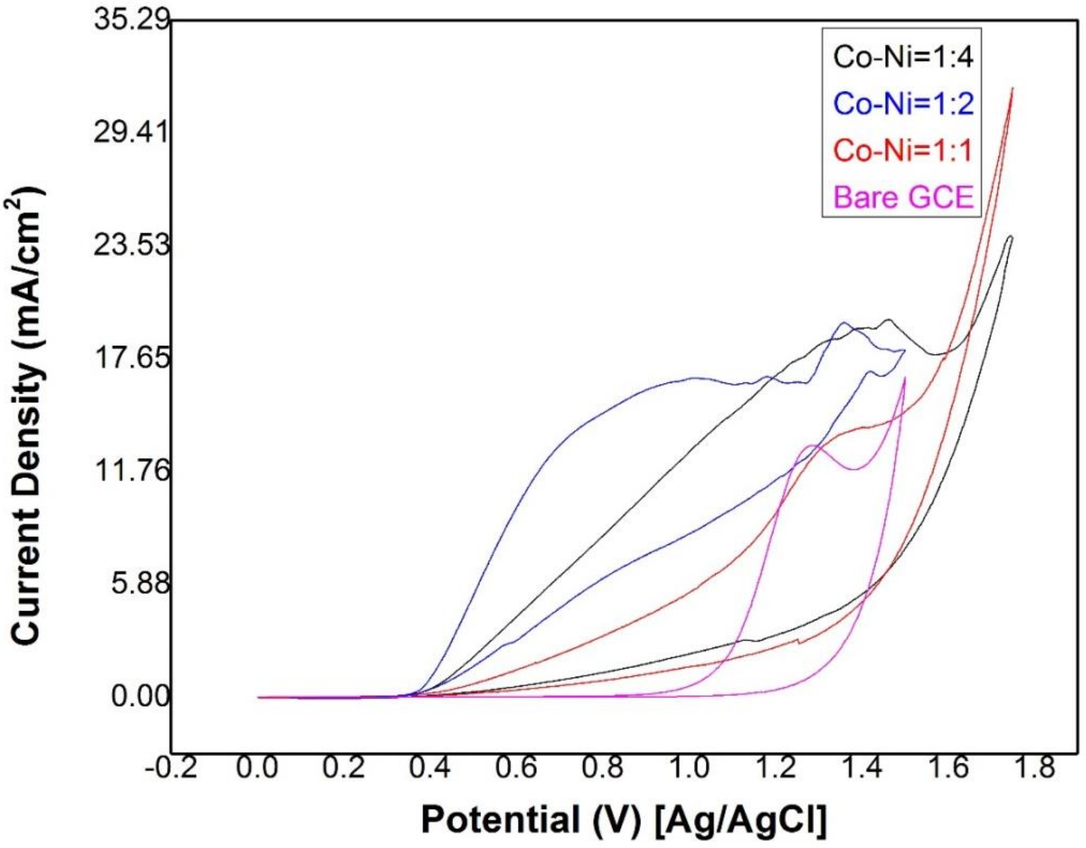


Figure 5.14: Comparison of Various Electro-catalysts on modified GCE

Table 5.2: Current Densities of Various Electro-catalyst on GCE electrode

Electro-catalysts	**Current Density (mA/cm^2)**
Bare Glassy Carbon Electrode	11.6
Co-Ni=1:1 with graphene on modified GCE	11.96
Co-Ni=1:2 with graphene on modified GCE	18
Co-Ni=1:4 with graphene on modified GCE	20

Conclusion

Graphene based bimetallic (Co-Ni=1:1, Co-Ni=1:2 and Co-Ni=1:4) electro-catalyst has been successfully synthesized through the simple solution synthesis method. All the prepared composites have shown face centered cubic structure.

SEM images shown that nickel and cobalt nanoparticles are uniformly dispersed over the graphene sheet.

Electrochemical properties of the prepared composites reveal high electro-catalytic activity toward methanol electro-oxidation. It has been concluded that graphene can be utilized as a supporter material to enhance electro-catalytic activity towards methanol due to its high electrical conductivity and excellent adsorption capacity.

Co_1-Ni_4 decorated graphene reveals the best results among the prepared electro-catalysts. It has been concluded that by increasing concentration of nickel nanoparticles could enhance electro-catalytic activity.

Recommendations

Graphene is one of the most promising candidate as an electrode material due to its electrical conductivity and excellent adsorption capacity. In this research graphene based bimetallic (Co-Ni) electro-catalyst with different composition (Co-Ni=1:1, Co-Ni=1:2 and Co-Ni=1:4) has been prepared by using simple solution synthesis method.

Although Co-Ni=1:4 showed significant electro-oxidation towards methanol but still it can be enhanced by changing the composition of Co-Ni. At the same time the amount of graphene can also be increase to get the desired current density. Calcination is also very important factor that can be utilized to achieve better results but calcination of composites should be in the argon atmosphere. Moreover, these composites should be analyzed by Electrochemical Impedance Spectroscopy (EIS).

Annexure –I

The IRES International Conference, Pune, India, 25th -26th January 2017

Development of Co-Ni/graphene based bimetallic electro-catalyst for methanol oxidation

Ehtsham Sarwar, Muhammad Irfan Raza, and Naseem Iqbal

US-Pakistan Center for Advance Studies in Energy(USPCAS-E)

NUST, Islamabad 44000,Pakistan

Abstract

Recently carbon black was commonly used as a support for fuel cells but their properties were not satisfactory for the better electro-catalytic activity and stability. However, graphene can overcome the main problem facing the non-precious electro-catalysts; low electro-catalytic activity. Commonly platinum based electrode materials were used in DMFCs, but high cost of platinum limited the commercialization of DMFCs. In this paper the electro-catalytic oxidation of methanol is studied on the non-noble catalysts Ni-Co/graphene. The bimetallic electro-catalyst was prepared with different Co-Ni ratios by using simple solution synthesis method. The synthesized materials are characterized by X- ray diffraction (XRD) and scanning electron microscopy (SEM). The electro-catalytic activity of Ni-Co/graphene has been investigated by using cyclic voltammetry.

Keywords: DMFCs, Graphene, Electro-catalyst, Electro-catalytic activity.

1. INTRODUCTION

Continuous depletion of fossil fuels day by day and increase in the energy demands encourage the researchers to focus on the renewable energy resources to fulfil energy demands and reduce the greenhouse gases such as SOx, NOx and CO_2. Among the renewable resources fuel cells are considered as a greener energy and alternative with almost zero pollutants. Basically, fuel cell is a device that converts chemical energy of fuel into electricity. Fuel cells have three main components such as anode, cathode and electrolyte. Fuel cell provides high electrical efficiency as compare to the other resources. Fuel cell is considered as efficient, environmental friendly, non-polluting, silent in operation because there are no any moving parts. There are various types of fuel cells differ from each other in terms of operating temperature, charge carrier, fuel and efficiency such as Polymer electrolyte membrane fuel cells (PEMFCs), Phosphoric acid fuel cells (PAFCs), Molten carbonate fuel cells (MCFCs), Alkaline fuel cells (AFCs), Solid oxide fuel cells (SOFCs) and Direct methanol fuel cells (DMFCs). Fuel cells are suitable for various applications such as military purpose, portable power, stationary power and transport. In fuel cells catalyst is the main factor which determines activity, stability and overall cost of the fuel cells. Among fuel cell types DMFCs are considered best for the oxidation of methanol and reduction of oxygen. Usually platinum is used as a catalyst in DMFCs but due to its high cost its commercialization becomes limited. The main problem with the platinum is its poor utilization efficiency which makes it not suitable for DMFCs [1-4]. In order to develop an electro-catalyst having low cost, high electro-catalytic activity and stability the energy researchers are focus on the development non- platinum based electro-catalysts for the stability of the electro-catalyst. Researchers reported that activity and stability of a catalyst could be enhanced utilizing graphene as a supporter material for methanol oxidation in methanol fuel cell. Graphene is the stronger material that can be utilized in the development of electrode materials due to its significant properties such as low production cost, unique structure, high thermal stability, high conductivity and larger surface area [5-7]. Nickel has been used in various studies due to its electrochemical stability and resistance to poisoning. But due to its poor electrical conductivity its use becomes limited, however researchers are now focusing to use additive materials to enhance its performance such as Nickel-modified manganese oxide [12] and Ni-MnO_x/C [11]. Various researchers have used cobalt as an additive material in order to enhance electro-catalytic performance. In this paper, we synthesize the non-noble bimetallic Co-Ni/Graphene electro-catalysts considering various Co-Ni ratios for the oxidation of methanol. The electrochemical properties of the prepared electro-catalysts are investigated by using cyclic voltammetry [13].

2. EXPERIMENTAL

2.1. Synthesis of Graphene oxide (GO)

Improve Hummer's method [8] has been used for the preparation of graphene oxide. In this method graphite powder is utilized for the preparation of graphene oxide. A beaker containing 50 (ml) sulphuric acid with a thermometer is placed in an ice bath. Sodium nitrate (0.6 grams) is added to sulphuric acid and stirring is performed. Then 1.3 (grams) of graphite is added which results in the formation of expanded graphite. Till this point the temperature of the reaction mixture is kept at 20°C. Then 3.8 (grams) of potassium permanganate were added. Now temperature was increased to 30°C from 20°C. After this warm deionized water (100 ml) was added drop wise. It should be assured that temperature should not be fall below 30°C. Then warm hydrogen peroxide was added to the mixture in order to get graphene oxide with impurities. To obtain pure GO, we have used centrifuge for cleaning. During cleaning, we have washed our mixture with ethanol and distilled water various times.

2.2. Synthesis of Ni-Co/graphene composites

Ni-Co/graphene composites have been synthesized using simple solution synthesis method [9]. Three electro-catalysts have been prepared at different Ni/Co ratios with graphene.

Table.3. Concentration of Nickel and Cobalt for composites

Electro-catalyst	Nickel (mmol)	Cobalt (mmol)	Graphene (mg)
Co_1-Ni_1/G	0.5	0.5	100
Co_1-Ni_2-/G	0.6	0.3	100
Co_1Ni_4/G	0.8	0.2	100

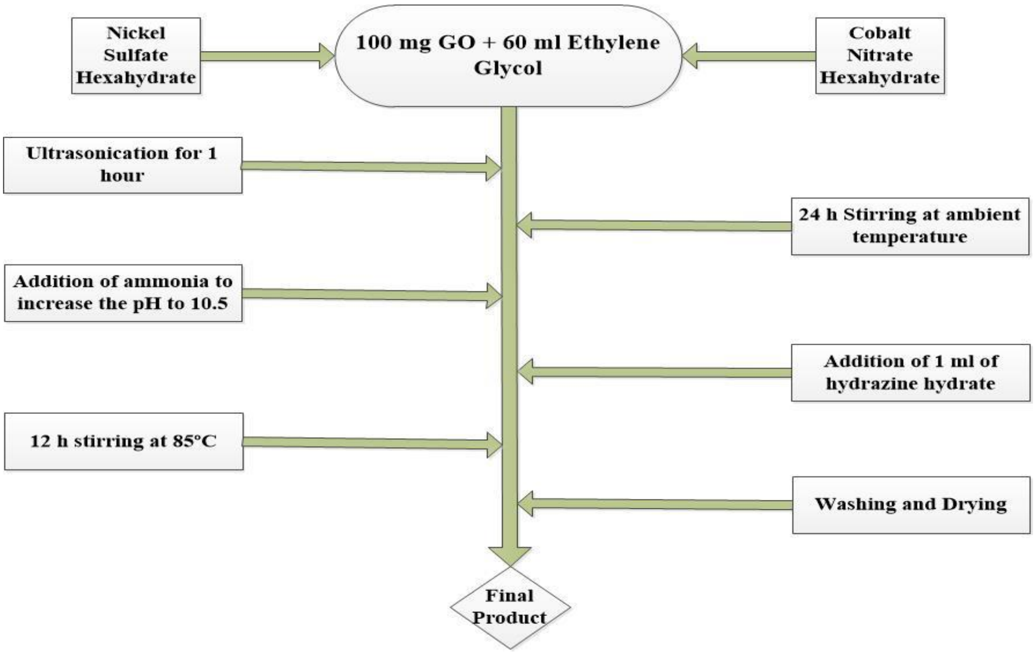


Fig.1. Flow diagram for the preparation of Co-Ni/G composites

2.3. Preparation of working electrode

For the preparation of working electrode, first of all platinum electrode was polished with the alumina slurry and then washed with distilled water and dried in air. Then slurry of 2 mg working material, 20 µl nafion solution and 400 µl isopropanol is formed. Then with the help of micro pipette about 15 µl of the slurry was deposit on the active area of working electrode and dried in open air [10].

3. RESULTS AND DISCUSSIONS

3.1. X-ray diffraction

The characteristic peak was obtained at 2θ of 11.5° which clearly indicates the formation of graphene oxide (GO) as shown in Fig. 2 (A). The X-ray diffraction analysis of Ni-Co/graphene shows intensity peaks at 2θ values of 37°, 43° and 62° clearly indicates the formation of nickel oxide or cobalt oxide or both, because nickel and cobalt have same crystal structure, successive atomic numbers, and closer molecular weights under normal conditions as shown in Fig. 2 (C). In this nanocomposite, there was no any peak indicating the formation of carbon because we have calcined the composite at 320°C and burning temperature of graphene is 350°C, so that we can say that only little amount of carbon was present in this composite which did not appear in the X-ray diffraction pattern. The other X-ray diffraction analysis of Ni-Co/graphene (B) without calcination shows intensity peaks at 2θ values of 21.69°, 37°, 43° and 62° can be assigned to the characteristic of Face-centered cubic structure, which clearly indicates the formation of pure nickel or pure cobalt or both, because nickel and cobalt have same molecular weights, successive atomic numbers, and same crystal in the normal conditions. On the other side, the X-ray pattern have a sharp peak at 21.69° which indicates the presence of carbon in composite as shown in Fig. 2 (B).

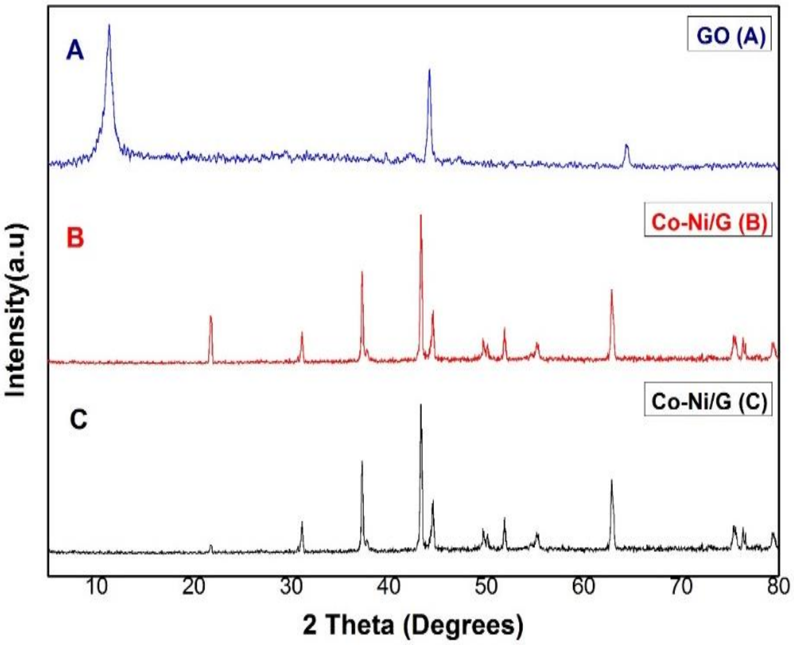


Fig.2. XRD Pattern of GO (A), Co-Ni/G (B) and Co-Ni/G (C) with calcination

3.2. Scanning Electron Microscope:

The SEM images below shows the morphology of the prepared graphene oxide and nanocomposites. In Fig.3. (a) wrinkles can be seen which shows the formation of graphene oxide. It can be seen in the Fig.3. (b), Fig.3. (c) and Fig.3. (d) that nickel and cobalt nanoparticles are uniformly dispersed over the sheet of graphene. However, Ni_4-Co_1/G nanocomposite shows that nanoparticles are more uniformly distributed then the Ni_1-Co_1/G and Ni_2-Co_1/G. This may be due to the presence of more concentration of nickel.

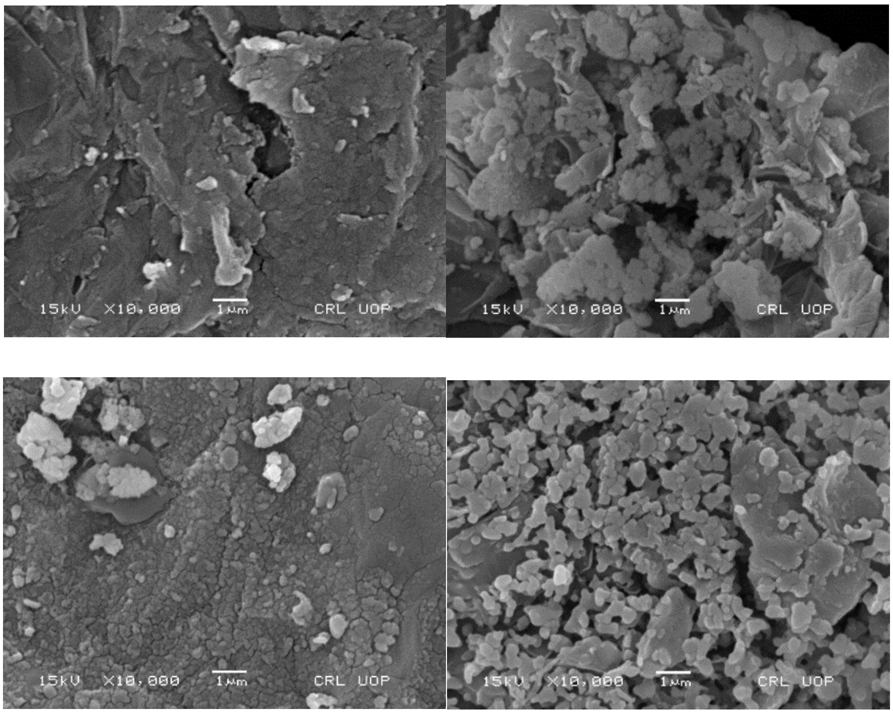


Fig.3. SEM image of GO (a), Ni1-Co1/G (b), Ni2-Co1/G (c) and Ni4-Co1/G (d)

3.3. Electrochemical properties of Ni-Co/graphene nanocomposites:

To investigate electro-catalytic activity of Co-Ni/graphene at various concentrations for methanol oxidation, cyclic voltammetry method was carried out in 1M KOH containing 3M methanol. The potential -800 mV to 200 mV is applied between the working electrode and the reference electrode while the current is measured against the applied potential. The current density measured for bare platinum was about 11.5 mA/cm^2. And the current density measured for Co_1-Ni_1/G, Co_1-Ni_2/G and Co_1-Ni_4/G was about 19.5, 40.0 and 60.0 mA/cm^2 as shown in the Fig.4. We observed that as we increase the concentration of nickel in our composite, current density also increases which leads to the formation of high electro-catalytic activity towards methanol oxidation. As can be seen from the Fig.4., Co_1-Ni_4/G has a better electro-catalytic activity as compare to the other prepared electro-catalysts because of its high current density.

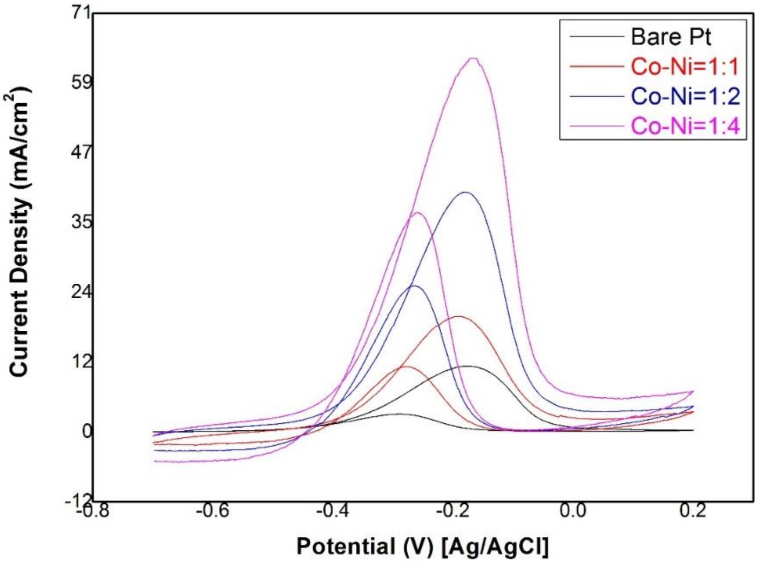


Fig.4. Cyclic Voltammograms at a scan rate of 50 mV/s for bare Pt and CO_x-Ni_y/G at various concentration.

Conclusion:

Graphene based bimetallic (Co-Ni) electro-catalyst has been successfully synthesized through the simple solution synthesis method. High electro-catalytic activity toward methanol electro-oxidation has been achieved. It has been concluded that graphene can be utilized as a supporter material to enhance electro-catalytic activity towards methanol due to its high electrical conductivity and excellent adsorption capacity. Co_1-Ni_4 decorated graphene reveals the best results among the prepared electro-catalysts. So, it has been concluded that as we increase the concentration of nickel, the current density tends to increase which leads to the oxidation of methanol.

References

1. Sharma, Surbhi, and Bruno G. Pollet. "Support materials for PEMFC and DMFC electrocatalysts—a review." Journal of Power Sources 208 (2012): 96-119.
2. Badwal, S. P. S., et al. "Direct ethanol fuel cells for transport and stationary applications–A comprehensive review." Applied Energy 145 (2015): 80-103.
3. Soo, Li Ting, et al. "An overview of the electrochemical performance of modified graphene used as an electrocatalyst and as a catalyst support in fuel cells." Applied Catalysis A: General 497 (2015): 198-210.
4. Jang, Hee Dong, et al. "Three-dimensional crumpled graphene-based platinum–gold alloy nanoparticle composites as superior electrocatalysts for direct methanol fuel cells." Carbon 93 (2015): 869-877.
5. Ma, Junhong, et al. "Enhanced electrocatalytic activity of Pt nanoparticles supported on functionalized graphene for methanol oxidation and oxygen reduction." Journal of colloid and interface science 457 (2015): 102-107.
6. Antolini, Ermete. "Graphene as a new carbon support for low-temperature fuel cell catalysts." Applied Catalysis B: Environmental 123 (2012): 52-68.
7. Huang, Huajie, et al. "Graphene nanoplate-Pt composite as a high performance electrocatalyst for direct methanol fuel cells." Journal of Power Sources 204 (2012): 46-52.
8. T.-T. Wu and J.-M. Ting, “Preparation and characteristics of graphene oxide and its thin films,” Surf. Coatings Technol., vol. 231, pp. 487–491, 2012.
9. Wang, Zaihua, et al. "High electrocatalytic activity of non-noble Ni-Co/graphene catalyst for direct ethanol fuel cells." Journal of Solid State Electrochemistry 17.1 (2013): 99-107.
10. Barakat, Nasser AM, and Moaaed Motlak. "Co x Ni y-decorated graphene as novel, stable and super effective non-precious electro-catalyst for methanol oxidation." Applied Catalysis B: Environmental 154 (2014): 221-231.

11. Hameed, RM Abdel. "Microwave irradiated Ni–MnO x/C as an electrocatalyst for methanol oxidation in KOH solution for fuel cell application." Applied Surface Science 357 (2015): 417-428.
12. Samant, Purnakala V., and Julio B. Fernandes. "Nickel-modified manganese oxide as an active electrocatalyst for oxidation of methanol in fuel cells." Journal of power sources 79.1 (1999): 114-118.
13. Xia, Yang, Yifu Yang, and Huixia Shao. "Differences in the effects of Co and CoO on the performance of Ni (OH) 2 electrode in Ni/MH power battery." Journal of Power Sources 196.1 (2011): 495-503.

Annexure –II

3rd International Conference on Innovative Engineering Technologies (ICIET'2016)
August 5-6, 2016 Bangkok (Thailand)

Graphene based Electro-catalysts for DMFCs

Ehtsham Sarwar, Muhammad Irfan Raza, and Naseem Iqbal

US-Pakistan Center for Advance Studies in Energy(USPCAS-E) NUST,
Islamabad 44000,Pakistan

Abstract

Fuel cell is a device that generates electricity by a chemical reaction. Recently carbon black was commonly used as a support for fuel cells but their properties were not satisfactory for the better electro-catalytic activity and stability. In the recent years, graphene is introduced as a carbon support that can replace the carbon black because it provides better resistance towards corrosion, high surface area, high mechanical strength, high conductivity. and potential low manufacturing cost. Commonly platinum based electrode materials were used in DMFCs, but high cost of platinum limited the commercialization of DMFCs. In this paper graphene supported Pt-based materials and graphene supported non-Pt metals are compared. Electro-catalytic activity of the electro-catalysts was compared through the comparison of I_F/I_R ratio and charge transfer resistance (R_{ct}) obtained from the cyclic voltammetry.

Keywords---Electro-catalysts, DMFCs, Graphene, Electro-catalytic activity, Stability

Introduction:

Due to increase in the energy demands day by day, continuous and rapid depletion of fossil fuels along with the increase in the concentration of greenhouse gases encourages the researchers to do research into the development of alternative and greener energy sources. As fuel cells, have almost zero emissions of harmful greenhouse gases like So_x, No_x and Co_2, which attracts the scientists and engineers to do research in the field of fuel cells. Basically. fuel cell is an electrochemical device that converts the chemical energy into electrical energy. Fuel cell is consisting of an anode, cathode and an electrolyte. Fuel cells have higher fuel conversion and electrical efficiency as compare to the conventional combustion. There are various types of fuel cells, which includes proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), phosphoric acid fuel cells (PAFCs), solid oxide fuel cells (SOFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs) and microbial fuel cells (MFCs). Fuel cells are very suitable for future transport, stationary and portable power applications along with the environmental benefits. Direct methanol fuel cells (DMFCs) are very effective in oxidizing methanol in the anodes and reducing oxygen in the cathodes. Catalyst is the main factor which determines the efficiency, activity and overall cost of the fuel cell device. Platinum is the most widely used electro-catalysts in the direct methanol fuel cells (DMFCs). Platinum catalysts are very attractive for DMFCs, but they are very expensive, poor utilization efficiency and limited platinum availability [1-4].

To develop a catalyst having better catalytic activity and stability, researchers are focused on the development of Pt based catalysts for the oxidation of methanol in DMFCs. On the other hand, to further improve the electrochemical activity and stability, various carbon materials have been reported as a support for fuel cells, such as carbon nanofiber, carbon nanotubes and mesoporous carbon**.** Graphene is a two-dimensional one-atom-thick planar sheet of sp^2 bonded carbon atoms; Compared with other carbon materials graphene is an ideal electrode material due to its high surface area, good thermal stability, unique graphitized basal planer structure, excellent conductivity and lower manufacturing cost. Production cost of graphene nanosheets is lower as compare to the other carbon nanotubes [5-7]**.** Graphene is a promising material for its potential applications in various fields such as solar cells, super capacitor and fuel cells [14].

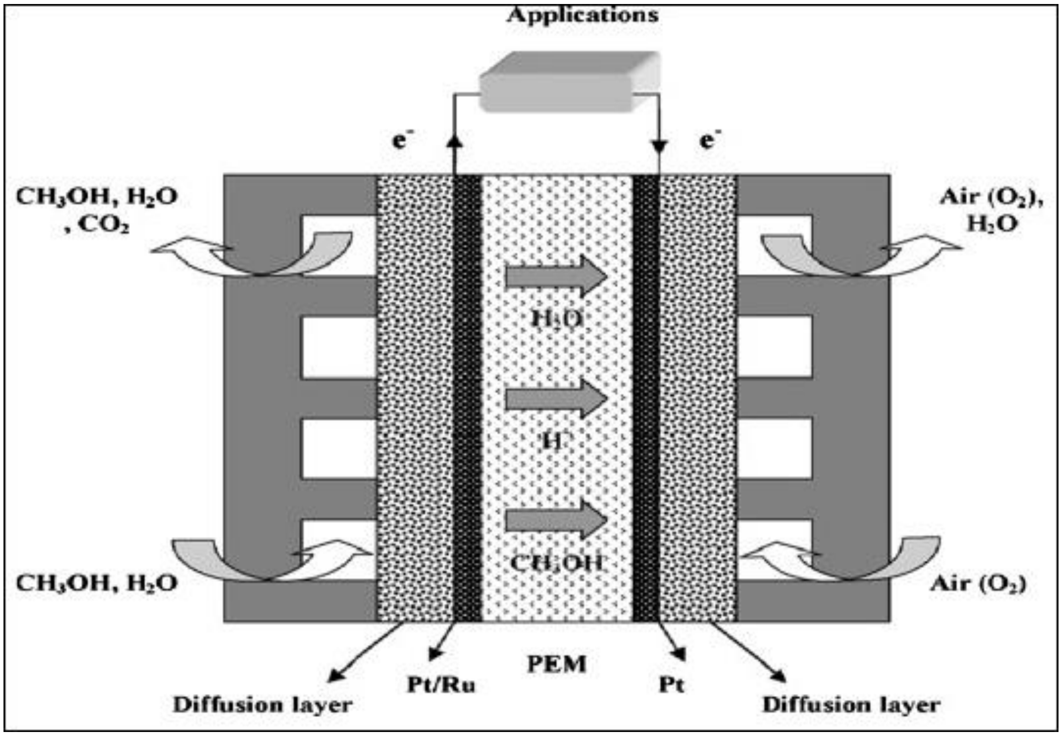


Figure.1 *Schematic diagram of DMFC [13].*

Synthesis of materials:

Graphene nanoplate-Pt composite was synthesized by using a soft chemical method to load platinum nanoparticles on graphene nanoplates. In a typical method ethylene glycol and $Pt(No_3)_2$ solution was added to the graphene nanoplates dispersion and stirring is performed for 15 min. After this the resulting mixture was then transferred to Teflon-lined stainless autoclave and sealed tightly, autoclave is then heated to 120ºC for 12 hours. After performing the solvothermal treatment, the nanocomposite is named as GNP/Pt and various cycles of centrifugation is performed, washed and then drying is performed in air at 60ºC overnight [7]. Graphene-CeO2 hybrid support for Pt nanoparticles was synthesized, graphene oxide was prepared by modified hummer's method. CeO_2-GN hybrid support was prepared by taking a specific amount of cerium nitrate and distribute in graphene oxide solution. Then adjust the pH of solution to 10 by using the ammonia. After this temperature is increased to 80ºC for 6 hours. Then mixture is transferred into an autoclave for the hydrothermal treatment at 160ºC for 4 hours. Finally, product was collected after filtering, washed with ethanol and water several times and then dried in a vacuum oven at 50ºC. Pt-CeO_2/GN was prepared by taking 45.2 mg of CeO_2/GN and dispersed into 50 ml ethylene glycol and ultrasonication is performed for one hour. After this 30 mg of H_2PtCl_6 was added, and set the pH of the solution to 9 with the addition of potassium hydroxide drop wise. Then stirred the mixture for 4 hours at 90ºC and Pt-CeO_2/GN electro-catalyst was collected [8]. Pt-SiO_2/Graphene nanocomposites was synthesized using solvothermal method, graphene oxide was prepared by modified Hummer's method. Pt-SiO_2/Graphene catalyst was prepared by taking the 10.2 ml of H_2PtCl_6 solution and inserted the solution into 20 ml DMF, containing graphene oxide (50 mg). Then stirring is performed, after this 0.15 g of KI and certain amount of TEOS were added into the solution and stirring is performed for one hour at room temperature. After this mixture was shifted into a 50 ml Teflon-lined stainless steel autoclave and heated at 130ºC for 5 hours. The solid product was collected after performing various cycles of centrifugation, washed with ultrapure water and ethanol several times and then dried for 24 h at 60ºC. Three different products were obtained and named as Pt-SiO_2/G-1, Pt-SiO_2/G-2 and Pt-SiO_2/G-3 for the initial amounts of 11.2, 18.6 and 31 mg TEOS. Similarly, SiO_2/G nanocomposite was also prepared in the same way as the composite of Pt-SiO_2/G but in the absence of H_2PtCl_6 for comparison, while a sample of Pt on graphene was also prepared without TEOS) [15]. PtCo nanoparticles supported on EG was synthesized**.** In order to prepare the EG, the natural graphite flakes were dipped in $HClO_4$ for 10 min, filtered and produced by using muffle furnace under 900-1000ºC. PtCo/EG catalyst was synthesized by the solution-phase reduction method. In this method, a total of 20 % metal weight of PtCo (with atomic ratio 1:1) catalyst was prepared by taking 29.44 mg of expanded graphite and dispersed in the solution of DI water (10 ml) and ethyl alcohol (10 ml) in an ultrasonic bath for 30 min, after this 1.0 ml of 0.0289 M H_2PtCl_6 solution and 0.1 ml of 0.289 M cobaltous chloride solution were mixed in the solution and stirring is performed for 10 min. Then pH value was adjusted to 10 using NaOH (0.5 M) solution, and then ethylene glycol was added and stirring is performed for 20 min. After this solution was stirred under the flow of argon at 140ºC for 3h. The resulting product was filtered, washed with DI water and ethanol several times, and finally dried for 24 h at

70ºC in a vacuum oven. Similarly, preparation of PtCo/MWCNT catalyst was completed following the same procedure [9]. Co-Ni-decorated graphene electro-catalyst was synthesized**.** Graphene oxide was prepared by a modified hummer's method. CoNi loaded graphene was obtained by taking a round flask, graphene oxide powder (300 mg) were dispersed in 400 ml distilled water and sonicated for 40 min. After this hydrazine hydrate (0.5 ml) was added to the solution. Certain amount from cobalt acetate and nickel acetate were individually dissolved in the water and mixed with graphene oxide suspension. In order to study the loading weight 0.1, 0.2 and 0.4 g from each salt were utilized. To study the influence of metallic nanoparticles composition, the loading weight was fixed at 0.4 g, the utilized NiAc:CoAc amounts (g:g) were 0.0:0.4, 0.1:0.3, 0.2:0.2 and 0.4:0.0. After this slurry was refluxed for 10 h at 150ºC. After this step the solution was filtered and filter cake was washed with water various times. Then dried the sample at 80ºC for one night under the vacuum oven. After this calcined the obtained product under argon atmosphere for 2 h at 850ºC [10]. Simultaneous Pt deposition and nitrogen doping electro-catalyst has been synthesized. GO was prepared from flaky graphite powder by using a modified Hummers method. For the preparation of electro-catalyst, GO solution was mixed with 9.2 (ml) of H_2PtCl_6, 0.1550 gram of sodium citrate ($Na_3C_6H_5O_7$) and 8 grams of urea(CH_4N_2O) and ultrasonicated for 2 hours. Then 8 ml of CH_2O_2 was added. After this, the mixture was sealed in a 100 (ml) Teflon-lined autoclave for 12 hours at 180ºC. Then leave the autoclave to cool down to room temperature naturally and reactant was washed several times with water and ethanol in order to remove impurities. Sample was dried under vacuum oven to obtain final product (Pt/N-Graphene). For the preparation of Pt/Graphene, the same procedure was followed in the absence of urea [11]. Reduced graphene oxide supported FePt alloy nanoparticles are synthesized by following two steps. In the first step 24 mg of $K_4Fe(CN)_6.3H_20$ is dissolved in 24 mL DI water. Then the solution is mixed into 6 mL GO solution under stirring. After this solution is ultrasonicated for 30 min and then transferred into a 40 (mL) autoclave and maintained at 180ºC for 24 hours. Then the product was washed with ethanol and water several times and dried for 12 h at 60ºC under vacuum. While in the second step 60 (mg) of the hydrothermal products are mixed into 60 (mL) $H_2PtCl_6.3H_2O$ solution. After this ultrasonication is performed for 30 min and then evaporated at 80ºC under stirring. After drying, the obtained powder was then inserted into the tube furnace and sintered for 2 h in H_2/Ar at 120ºC with the heating rate of about 1ºC/min to obtain the final product (FePt/RGO). Similarly, for comparison 6mL (GO) solution is mixed with 60 mL $(H_2PtCl_6).3H_2O$ solution. After this ultrasonication is performed for 30 min and stirring is performed at 80ºC. After this calcination is performed at 120ºC in H_2/Ar atmosphere to obtain the final product (Pt/RGO) [12].

Electrochemical Properties

Basically, there are three main factors, that can be considered in order to observe the electro-catalytic activity of the synthesized electro-catalyst named as ECSA (Electrochemical surface area), I_F/I_R ratio and R_{ct} (charge transfer resistance).

Table I Electrochemical properties of various electro-catalysts

Electrode	ECSA (m^2g^{-1})	I_F ($mAcm^{-2}$)	I_R ($mAcm^{-2}$)	I_F/I_R ratio	R_{ct} (ohm)	References
GNP/Pt	63.0	57.7	47.5	1.21	473.5	[7]
XC-72/Pt	33.7	17.5	15.1	0.86	4.5	[7]
RGO/Pt	53.6	44.2	52.1	0.85	15.0	[7]
Pt/GN	53.9	185.8	-	1.37	-	[8]
Pt7% CeO_2/GN	66.4	440.1	-	1.48	-	[8]
Pt5% CeO_2/GN	62.5	324.8	-	1.45	-	[8]
Pt3% CeO_2/GN	59.1	279.5	-	1.41	-	[8]
Pt10% CeO_2/GN	45.3	402.9	-	1.35	-	[8]
Pt-SiO_2/G-2	87.19	1047	1010	1.04	-	[15]
Pt-SiO_2/G-3	51.30	320	313	1.02	-	[15]
Pt-SiO_2/G-1	62.53	520	483	1.08	-	[15]
Pt/G	41.29	248	225	1.10	-	[15]
Pt/C	38.87	320.75	-	0.74	-	[9]
PtCo/EG	55.75	525.08	-	1.17	-	[9]
PtCo/MWCNT	44.83	474.59	-	1.14	-	[9]
Co-Gr	-	-	-	-	5.128	[10]
$Co_{0.2}Ni_{0.2}$-Gr	-	-	-	-	2.824	[10]
Ni-Gr	-	-	-	-	5.788	[10]

Pt-G	65.60	-	-	1.0	-	[11]
Pt-NG	78.55	-	-	1.1	-	[11]
Pt/RGO	-	-	-	1.75	-	[12]
FePt/RGO	-	-	-	2.26	-	[12]

It has been concluded that GNP/Pt has better electro-catalytic activity and stability, since GNP/Pt has higher value of I_F/I_R ratio and smaller value of charge transfer resistance as compare to the RGO/Pt and XC-72/Pt for methanol oxidation [7].

Pt-CeO_2/GN electro-catalyst has been prepared using two different methods consisting of hydrothermal method and impregnation-chemical reduction method. It has been concluded that the largest ESA and I_F/I_R ratio with the CeO_2 content of 7 wt% had the best performance as compare to the other catalysts for the oxidation of methanol [8].

Pt-SiO_2/G electro-catalyst were synthesized successfully by a one-pot method under solvothermal condition. The electrochemical measurements showed that the Pt-SiO_2/G-2 had the highest value of ECSA and performs best as compare to the other catalysts for the electrooxidation of methanol. It has been concluded that for this catalyst, methanol electrooxidation was improved by 4.2 times and the stability of this catalyst also improved by 1.64 times as compare to the Pt/G catalysts [15].

PtCo/MWCNT and PtCo-EG catalysts were successfully synthesized by using solution-phase reduction method. It has been concluded that PtCo nanoparticles supported on EG showed higher value of ECSA, larger value of I_F/I_R, more stability and excellent electro-catalytic activity towards the methanol oxidation as compare to the Pt/C and PtCo/MWCNT catalysts [9].

Co-Ni decorated graphene electro-catalysts were successfully synthesized. It has been concluded that better chemical corrosion resistance and high electro-catalytic activity toward methanol electrooxidation can be obtained through the Co-Ni decorated graphene electro-catalysts. In order to produce solid solution Co-Ni alloy nanoparticle, calcination of resultant decorated graphene in argon atmosphere is a very important step. It has been observed that $Co_{0.2}Ni_{0.2}$-decorated graphene showed the best results as compare to the other CoNi-decorated graphene metal loadings [10].

Pt-NG and Pt-G has been synthesized successfully. It has been observed that Pt-NG shows better electro-catalytic activity towards methanol considering both the mass and specific activities as compare to the Pt-G [11].

Pt/RGO and Fe-Pt/RGO has been synthesized and concluded that Fe-Pt/RGO shows higher value of I_F/I_R ratio, which means that Fe-Pt/RGO have better electro-catalytic activity as compare to the Pt/RGO [12].

Conclusion:

Commercialization of fuel cells is limited due to high cost of platinum and low stability of carbon supports. Graphene is a promising support material or catalyst materials in DMFCs which play a very important role for the oxidation of methanol in terms of electro-catalytic activity and stability. I_F/I_R and R_{ct} are the main factors which are obtained from cyclic voltammetry are responsible for the showing of electro-catalyst performance. A higher value I_F/I_R and the smaller value of R_{ct} indicate better oxidation of methanol.

1. It has been observed that when GNP/Platinum was synthesized, it shows I_F/I_R ratio equivalent to 1.21.
2. When the Pt-7%CeO2/GN was synthesized, it shows I_F/I_R ratio equivalent to 1.48.
3. When Pt-SiO_2/G-2 electro-catalyst was synthesized, it shows ECSA (m^2g^{-1}) value equivalent to 87.19 which is much better than the Pt/G.
4. Similarly, when PtCo/EG electro-catalyst was synthesized, it shows I_F/I_R ratio equivalent to 1.17.
5. When $Co_{0.2}Ni_{0.2}$-Gr was synthesized, it shows minimum charge transfer resistances that were 12.09, 3.168 and 2.824 at different methanol concentrations of 1.0, 2.0 and 3.0 as compare to the other CoNi-Gr metal loadings.
6. When Pt-NG electro-catalyst was synthesized, it shows higher ECSA value and larger I_F/I_R value.

7. Similarly, when Fe-Pt/RGO electro-catalyst was synthesized, it shows higher I_F/I_R value that was 2.26.

   Comparing seven different electro-catalyst, it was observed that $Co_{0.2}Ni_{0.2}$-Gr has showed significant results towards methanol oxidation as compare to the other four electro-catalyst reported earlier. $Co_{0.2}Ni_{0.2}$-Gr electro-catalyst has good stability and non-precious electro-catalyst. It is recommended that instead of using platinum which is very expensive metal with graphene, we should focus on non-noble metals with graphene because they can be synthesized in low cost as compare to the platinum and can give comparable electro-catalytic activity and stability.

References

[1] Sharma, Surbhi, and Bruno G. Pollet. "Support materials for PEMFC and DMFC electrocatalysts—a review." Journal of Power Sources 208 (2012): 96-119.

[2] Badwal, S. P. S., et al. "Direct ethanol fuel cells for transport and stationary applications–A comprehensive review." Applied Energy 145 (2015): 80-103.

[3] Soo, Li Ting, et al. "An overview of the electrochemical performance of modified graphene used as an electrocatalyst and as a catalyst support in fuel cells." Applied Catalysis A: General 497 (2015): 198-210.

[4] Jang, Hee Dong, et al. "Three-dimensional crumpled graphene-based platinum–gold alloy nanoparticle composites as superior electrocatalysts for direct methanol fuel cells." Carbon 93 (2015): 869-877.

[5] Ma, Junhong, et al. "Enhanced electrocatalytic activity of Pt nanoparticles supported on functionalized graphene for methanol oxidation and oxygen reduction." Journal of colloid and interface science 457 (2015): 102-107.

[6] Antolini, Ermete. "Graphene as a new carbon support for low-temperature fuel cell catalysts." Applied Catalysis B: Environmental 123 (2012): 52-68.

[7] Huang, Huajie, et al. "Graphene nanoplate-Pt composite as a high performance electrocatalyst for direct methanol fuel cells." Journal of Power Sources 204 (2012): 46-52.

[8] Yu, Shuping, et al. "Graphene–CeO 2 hybrid support for Pt nanoparticles as potential electrocatalyst for direct methanol fuel cells." Electrochimica Acta94 (2013): 245-251.

[9] Chen, Maojun, et al. "PtCo nanoparticles supported on expanded graphite as electrocatalyst for direct methanol fuel cell." Electrochimica Acta 165 (2015): 105-109.

[10] Barakat, Nasser AM, and Moaaed Motlak. "Co x Ni y-decorated graphene as novel, stable and super effective non-precious electro-catalyst for methanol oxidation." Applied Catalysis B: Environmental 154 (2014): 221-231.

[11] Tao, Li, et al. "Simultaneous Pt deposition and nitrogen doping of graphene as efficient and durable electrocatalysts for methanol oxidation."International Journal of Hydrogen Energy 40.41 (2015): 14371-14377.

[12] Guo, Jinxue, et al. "FePt nanoalloys anchored reduced graphene oxide as high-performance electrocatalysts for formic acid and methanol oxidation."Journal of Alloys and Compounds 604 (2014): 286-291.

[13] Kamaruddin, M. Z. F., et al. "An overview of fuel management in direct methanol fuel cells." Renewable and Sustainable Energy Reviews 24 (2013): 557-565.

[14] Ji, Kai, et al. "Efficient and clean synthesis of graphene supported platinum nanoclusters and its application in direct methanol fuel cell." Electrochimica Acta 85 (2012): 84-89.

[15] Vu, Thu Ha Thi, et al. "Solvothermal synthesis of Pt-SiO 2/graphene nanocomposites as efficient electrocatalyst for methanol oxidation."Electrochimica Acta 161 (2015): 335-342.