

# **Synthesis of Graphene based Non-Noble Metal electro-catalyst for Fuel cell applications**



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**Session 2014-16**

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**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**

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**August, 2017**

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## **Abstract**

Energy is considered to be a vital element for the economic growth and development of any country in the world. During the last few decades much attention is given to the alternative energy resources because conventional power generation is main cause of global warming. There are many alternative energy harnessing technologies including fuel cells. Fuel cells converts the chemical energy of the fuel into electrical energy by producing heat and water as by product. In the family of fuel cell, direct methanol fuel cell is considered very important because of methanol fuel. Compared with hydrogen methanol is abundant and easily transported liquid fuel. It has been observed that major problems associated with methanol fuel cells are methanol cross over and slow anode kinetics. By developing new material as anode catalyst reaction kinetics of the fuel cell can be improved. Two major challenges associated with anode catalysts are cost and performance analysis which are very important for the successful operation of DMFC. In DMFC mostly platinum and alloy catalyst are used for the electrooxidation of methanol. Several problems are associated with platinum base catalysts including higher cost and CO adsorption on the surface of the platinum. In order to overcome these challenges researchers are developing new effective and low cost electro-catalyst as a substitute of Pt-based catalysts for direct methanol fuel cells (DMFCs). Due to their oxidation properties nickel and cobalt show excellent electroanalytic properties. Both nickel and cobalt are popular transition metals have wide application as electro catalysts in fuel cells. Graphene is widely used carbon support material in fuel cell due to its high surface area and excellent conductivity. Currently the research is focused to develop non-noble metals electro-catalyst to replace the expensive noble metal electro-catalyst. However non noble metals such as Ni, Co, Pb, and W have limited catalytic potential. Electrocatalytic properties of these metals can be enhanced manifolds by depositing them on graphene sheets. In the present work we synthesized Ni/graphene and Co/graphene nanoparticle by simple solution synthesis method. The synthesized catalysts were characterized by X-ray diffraction, scanning electron microscopy and EDX. The electrocatalytic potential of the synthesized catalyst for methanol oxidation was investigated by cyclic voltammetry.

**Keywords:** Graphene, Graphene oxide, Direct methanol fuel cells, Nanocomposites, Electrocatalysts, Methanol oxidation, Cyclic Voltammetry

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## **List of Publication**

1. Muhammad Irfan Raza Naseem Iqbal, Tayyaba Noor, Ehtsham Sarwar, “Synthesis of graphene supported cobalt nanocomposites and their applications for methanol oxidation in alkaline medium” RJ\_Electrochemistry\_submission confirmation\_RJE-2017-E-088\*.

\*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
EDX	Energy Dispersive X-ray spectroscopy

# Chapter 1

## Introduction

### 1.1 Energy and Sustainable development

Sustainable development involves four key factors in terms of social, environmental, economic and energy resources sustainability under the global sustainability prospective. Therefore, energy derives the global economy and is considered as key element for the climate and the sustainable development. Sustainable development requires sustainable supply of clean and cheap sources of energy that do not have adverse social and environmental impacts [1-2].

Globally, about 87% of our total energy is produced by fossil fuel about 6% is generated in nuclear power plants and only 7% comes from renewable resources (hydro, wind, solar, geothermal and biofuel). Unfortunately, this planet has limited amount of fossil and nuclear energy resource and at the same time generation of energy can contribute to degradation of local environment such as global warming, acid rain and ozone layer depletion ultimately the climate change [3-4].

In order to get rid of all these critical challenges of energy security and environmental degradation attempts have been made in the development of advance, affordable and environment friendly energy harnessing technologies. In this regard, innovative energy technologies have got considerable attention during the last few decades. Among them fuel cell is considered as promising power generation technology both for mobile and stationary applications [5].

### 1.2 What is Fuel cell?

Fuel cell is an electrochemical device that converts chemical energy of the fuel directly into electrical energy. The working of a fuel cell is similar to a battery made up of an electrolyte placed between electrodes an anode and cathode. Unlike a typical battery fuel cell does not require recharging. It produces energy both electricity and heat with continuous supply of fuel. Oxygen and hydrogen are passed through electrodes, generating electricity, heat and water [6].

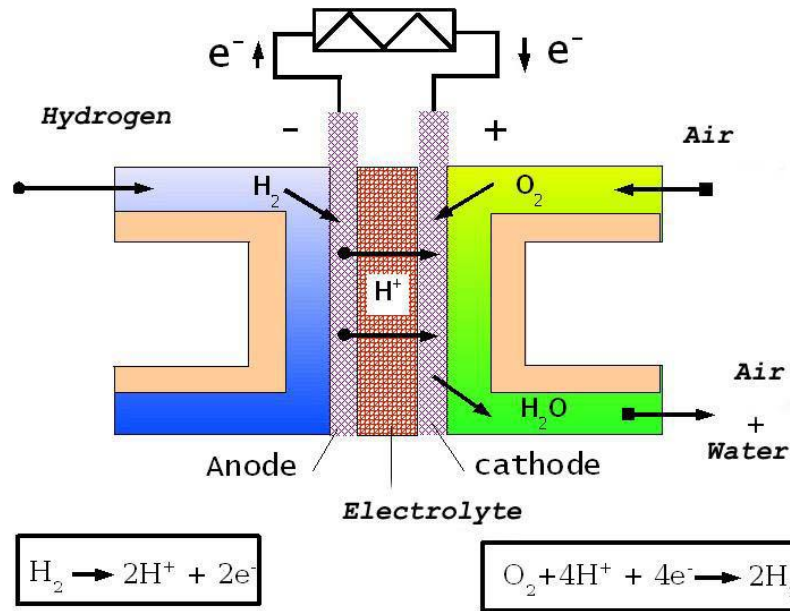
### 1.2.1 History and evolution of fuel cells

The invention of the fuel cell dates back from the middle of 19<sup>th</sup> century. A German scientist Christian Friedrich Shoenbein discovered the fuel cell effect by reporting that electrical current is generated by electrochemical reaction between oxygen and hydrogen. Simultaneously a Welsh scientist William Robert Grove who was in close contact with Christian Friedrich Shoenbein developed the first practical fuel cell, which he named the “gas voltaic battery”. Grove is well-thought-out to be the father of the fuel cell. Later on, in 1889, Ludwing Mond and his assistant Carl Langer introduced gas-powered battery using coal derived Mound-gas that attained 6 amps per square foot at 0.73 volts by using thin perforated platinum electrode. They termed their system a fuel cell. In 1893, Friedrich Wilhelm Oswald experimentally described the function of various components of fuel cell. He provided the theoretical understanding of fuel cell operation: electrode, electrolyte, oxidizing and reducing agents, anion, and cations. In 1900s, first practical hydrogen-oxygen fuel cell was developed by Francis Thomas Bacon [7-9]. In late1930, Francis Thomas Bacon developed first alkaline fuel cell that was used in NASA Apollo Spacecraft to provide both electricity and drinking water. In early 1990s, the direct methanol fuel cell was developed by the combine efforts of NASA jet propulsion laboratory and University of Southern California (USC). Since 2007, fuel cells are commercialized and are being used in different types of stationary and portable energy applications such as mobile phones, electric vehicles, and small power plants [10-11].

### 1.2.2 Fuel cell basic principle

A fuel cell contains three main components a fuel anode an oxidant cathode and an electrolyte membrane sandwich in between them [12]. Generally electrodes consist of porous materials shielded with layer of catalysts platinum in case of (PEMFCs) Fig. 1.1 illustrates the basic operational process of a typical PEMFC. At the anode molecular hydrogen (H<sub>2</sub>) is delivered from a gas-flow stream. The hydrogen is oxidized into hydrogen ions and electrons following electrochemical reaction takes place at the anode as shown in the equation (1.1).





**Figure. 1.1** Schematic representation of typical PEM fuel cell operation [13].

The hydrogen ions are migrated through the acidic electrolyte and electrons are forced to move through an external circuit all the way to cathode. At the cathode, electrons and the hydrogen ions, reacts with the oxygen which is supplied from an external gas-flow stream to form water as shown in the Figure. 2. The following electrochemical reaction takes place at the cathode as shown in the equation (1.2) [14].



The overall electrochemical reaction in the fuel cell produces water, heat and electrical energy as described in equation (3):



### 1.2.3 Classification of fuel cell technologies

Fuel cells are generally classified on the basis of electrolyte used in the fuel cell and by considering the working temperature of each of the cell. On the basis of working temperature there are two major categories of fuel cell low- temperature and high-temperature fuel cells. Low temperature fuel cells include the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Fuel Cell (PEMFC), the Direct Methanol Fuel Cell (DMFC) and



the Phosphoric Acid Fuel Cell (PAC). The high temperature fuel cell includes the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). They operate at the temperature approximately 600-1000 °C. A complete overview of different types of fuel cell is given in the Table 1.1

**Table 1.1** Comparison of different types of fuel cells [15-18].

	AFC	PEMFC	DMFC	PAFC	MCFC	SOFC
<b>Operating temp. (°C)</b>	<100	60-120	60-120	160-220	600-800	800-1000
<b>Applications</b>	Transportation, Space, Military, Energy storage system			Combined heat and power	Stationary power systems and transportation	
<b>Power Capacity</b>	50-150kW	50-250kW	5kW	50kW-11MW	100kW-2MW	100-250kW
<b>Charge Carrier in the Electrolyte</b>	OH <sup>-</sup>	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>	CO <sub>3</sub> <sup>2-</sup>	O <sup>2-</sup>
<b>Fuel</b>	H <sub>2</sub>	H <sub>2</sub>	CH <sub>3</sub> OH	H <sub>2</sub>	H <sub>2</sub> , CO, hydrocarbon	H <sub>2</sub> , CO, hydrocarbon
<b>Efficiency</b>	35~50	35~60	35~60	35~45	45~55	50~60

### 1.3 Direct Methanol Fuel Cells (DMFCs)

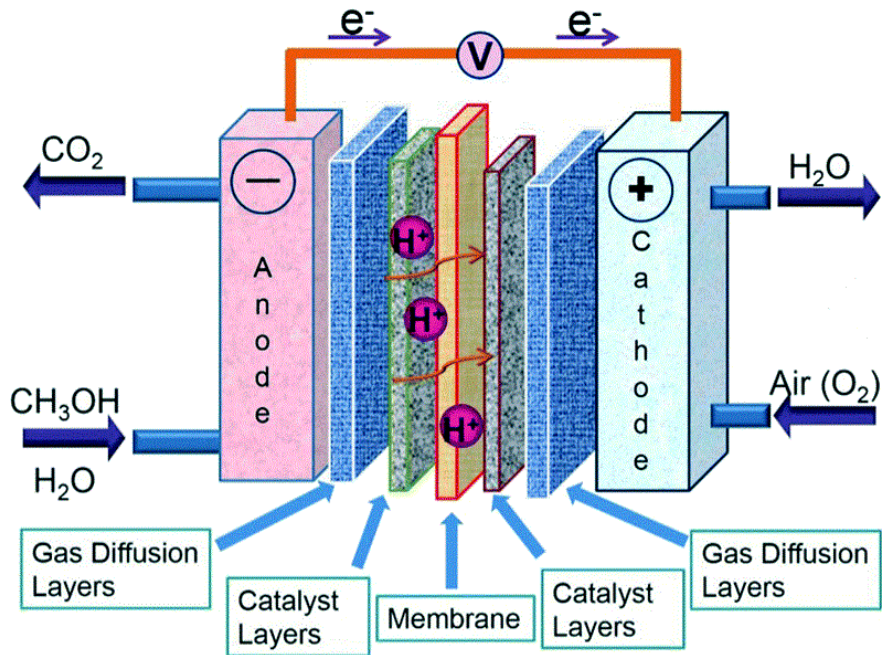
Fuel cells are considered promising power generation sources for mobile, stationary and portable applications. Particularly Direct Methanol fuel cell is among them that is widely studied over the past few a decade. In 1990, DMFC was developed by the combined efforts of NASA Jet Propulsion Laboratory and University of Southern California Direct methanol fuel cells (DMFCs) are classified as proton exchange membrane fuel cell in which methanol is directly used as fuel instead of hydrogen. Direct Methanol fuel cell has certain advantages over other fuel cell types because of its compact design, high power density, and low operating temperature. In Direct Methanol Fuel cell methanol is directly fed and oxidized at the anode without any further chemical conversion while at the cathode oxygen is reduced. This feature eliminates the hectic problem of hydrogen

production and purification. As compared to hydrogen methanol as fuel has various advantages such as transportation and storage [19-20].

### **1.3.1 Structure of Membrane Electrode Assembly (DMFCs)**

The heart of direct methanol fuel cell is the membrane electrode assembly (MEA) which consists of five important parts: Catalyst layer and diffusion layers of anode, cathode catalyst and diffusion layer in between them is the electrolyte membrane. Catalytic layer is often composed of carbon supported Pt or PtRu materials both at the anode and cathode. PEM membrane consist of perflourosulfonic acid polymer, currently Nafion membrane is being used. The diffusion layer is made up of Teflon with hydrophobic in nature to support the escape of CO<sub>2</sub> from anode. All these components combine to form a single cell. Multiple such cells combine to form fuel cell stack to deliver electrical power to external load [21].

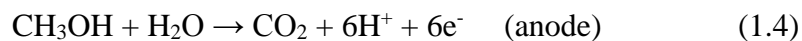
A schematic diagram of construction of membrane electrode assembly of DMFC is shown in Fig.1.2.



**Figure 1.2** Typical MEA Structure of DMFC [22]

### 1.3.2 Working Principle of DMFCs

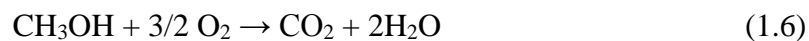
In direct methanol fuel cell methanol and water mixture are directly applied at the anode. Methanol is oxidized into  $\text{CO}_2$  and six electrons are released which are delivered to the external circuit for electrical work. Following reaction takes place at the anode as shown in equation (1.4)



Reduction of oxidation takes place at the cathode to form water as show in the equation (1.5)



The overall electrochemical oxidation of methanol into  $\text{CO}_2$  and water is as shown in the equation (1.6)



The thermodynamic efficiencies of the overall reaction can be calculated from the Gibbs free energy that is the ratio of maximum amount of electrical work ( $\Delta G^\circ$ ) and the total available energy the enthalpy ( $\Delta H^\circ$ ).

$$H_{rev} = \Delta G^\circ / \Delta H^\circ \quad (1.7)$$

The estimated free energy and electromotive force related to this overall reaction process with feeding pure oxygen under normal conditions (25°C and 1atm ) are

$$\Delta G = -686 \text{ KJ mol}^{-1} \quad \Delta E = 1.18\text{V} \quad (1.8)$$

The electro-oxidation of methanol in typical DMFC is shown in Fig. 1.3[23-25]

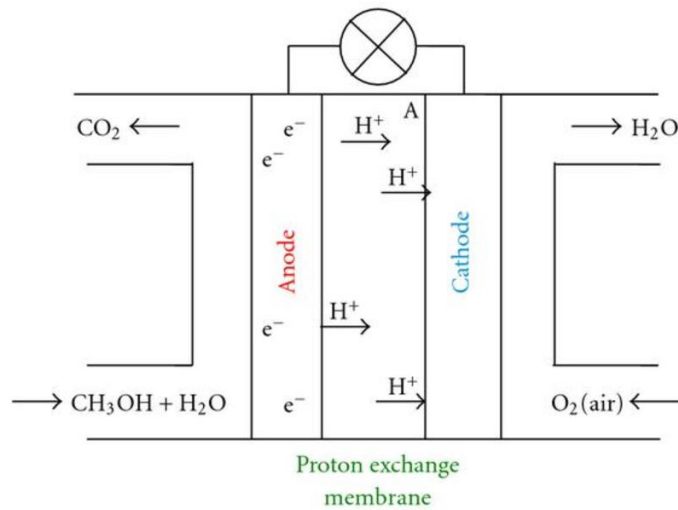


Figure. 1.3 Schematic diagram of reaction mechanism in DMFC [23-25].

#### 1.4 Current issues in DMFCs

In order to be competitive as a viable power source in the energy market some critical challenges associated with DMFCs must be solved. A few challenging problems to the improvement of such systems includes:

- High cost of noble metal electro-catalyst both for the anode and cathode
- A suitable electro-catalyst which can efficiently enhance the electro-oxidation of methanol at the anode
- An electrolyte membrane with high ionic conductivity and must be capable of low methanol cross over.
- A highly active electro-catalyst for oxygen reduction and must be methanol tolerant.
- High cost of presently used nafion membrane
- Poisoning of electro-catalyst by the intermediate species like CO
- Methanol cross over from the anode to cathode region which cause the degradation of the electrodes.

## **1.5 Objectives of this research**

Direct methanol fuel cells are low temperature fuel cell. Mostly pure Platinum (Pt) or alloys of Pt are used for the electrochemical conversion of fuel at the anode and oxygen reduction at cathode. The high cost of expensive materials for fuel cell catalyst ultimately increases total cost of the fuel cell which is the major problem in the successful commercialization of direct methanol fuel cell [26-27]. These problems can be solved in two ways

- (i) by replacing the expensive Pt metal with some suitable low cost non-noble metal
- (ii) by introducing new catalytic support material for enhanced electrical conductance

## **Summary**

Energy is considered as key input to the economy and sustainable development. There are many environmental issues related to the production of energy which are hazardous to the local environment. Thus, it is very important to adopt clean and environmental friendly method of energy generation. Fuel cells are electrochemical devices that convert the chemical energy into electrical energy without producing any pollutant to the environment. There are different types of fuel cell classified on the basis of temperature and type of fuel used. But however, direct methanol fuel cells have got much attention during the last decade. In DMFCs methanol is used as fuel instead of hydrogen which is easily stored and transported liquid fuel. DMFCs have high power densities and low operating cost as compared to other fuel cells.

## References

- [1] I. Dincer, “Environmental and sustainability aspects of hydrogen and fuel cell systems,” no. August 2006, pp. 29–55, 2007.
- [2] I. Transactions, E. Conversion, and S. Univer, “Environmental Impacts of Electricity Generation : A Global Perspective Environmental Impacts of Electricity Generation :,” no. September, 2016.
- [3] B. K. Bose, “Energy, Environmental Pollution, and the Impact of Power Electronics,” no. March, pp. 6–17, 2010.
- [4] A. R. Mohamed and K. T. L. Å, “Energy for sustainable development in Malaysia : Energy policy and alternative energy,” vol. 34, no. 2006, pp. 2388–2397, 2010.
- [5] O. Z. Sharaf and M. F. Orhan, “An overview of fuel cell technology : Fundamentals and applications,” *Renew. Sustain. Energy Rev.*, vol. 32, pp. 810–853, 2014.
- [6] B. L. Carrette, K. A. Friedrich, and U. Stimming, “Fuel Cells ± Fundamentals and Applications,” no. 1, pp. 5–39, 2001.
- [7] E. I. Ortiz-rivera, M. Ieee, A. L. Reyes-hernandez, I. S. Member, R. A. Febo, and I. S. Member, “Understanding the History of Fuel Cells,” vol. 2, no. 2, pp. 117–122, 2007.
- [8] A. S. Aricò, S. Srinivasan, and V. Antonucci, “DMFCs : From Fundamental Aspects to Technology Development,” no. 2, pp. 133–161, 2001.
- [9] S. R. Narayanan, T. I. Valdez, A. Kindler, C. Witham, S. Sursmpudi, and H. Frank, “CHALLENGES AND PROSPECTS,” pp. 33–36.
- [10] H. Liu, C. Song, L. Zhang, and J. Zhang, “A review of anode catalysis in the direct methanol fuel cell,” no. April, 2006.
- [11] R. Belot and F. Picard, “The Three Ages of Fuel Cell Research in France : A Socio-Technical System ’ s Resistance to Change ~,” vol. 2013, no. 3, pp. 525–

532, 2014.

- [12] R. H. Wolk, “for homes and hospitals.”
- [13] F. Barbir, “PEM Fuel Cells.”
- [14] J. Park, J. Kim, Y. Seo, D. Yu, H. Cho, and S. J. Bae, “Operating Temperature Dependency on Performance Degradation of Direct Methanol Fuel Cells,” no. 3, pp. 426–438, 2012.
- [15] S. Wasmus and A. Ku, “Methanol oxidation and direct methanol fuel cells : a selective review 1,” vol. 461, pp. 14–31, 1999.
- [16] Z. Wang, Y. Du, F. Zhang, Z. Zheng, Y. Zhang, and C. Wang, “High electrocatalytic activity of non-noble Ni-Co/graphene catalyst for direct ethanol fuel cells.,” *Sect. Title Electrochem. Radiational, Therm. Energy Technol.*, vol. 17, no. 1, pp. 99–107, 2013.
- [17] M. F. Cell, “Review Methanol Fuel Cell,” vol. 24, pp. 1223–1233, 2001.
- [18] T. Eren, N. Atar, and H. Saral, “Direct-methanol Fuel Cell Based on Functionalized Graphene Oxide with Mono-metallic and Bi-metallic Nanoparticles : Electrochemical Performances of Nanomaterials for Methanol Oxidation,” pp. 570–579, 2016.
- [19] R. Anahara and S. U. M. Yokokawa, “Present Status and Future Prospects for Fuel Cell Power Systems,” vol. 81, no. 3, 1993.
- [20] S. Mekhilef, R. Saidur, and A. Safari, “Comparative study of different fuel cell technologies,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 1, pp. 981–989, 2012.
- [21] G. A. Hards, “Direct Methanol Fuel Cells,” no. 1, pp. 150–159, 1996.
- [22] R. Liu and E. S. Smotkin, “Array membrane electrode assemblies for high throughput screening of direct methanol fuel cell anode catalysts,” vol. 535, pp. 49–55, 2002.
- [23] A. S. Aricò, V. Baglio, and V. Antonucci, “Direct Methanol Fuel Cells : History , Status and Perspectives,” 2009.



- [24] V. V Joshi and M. B. Patil, “— Recent Developments and Trends in Direct Methanol Fuel,” vol. 5, no. 3, pp. 3–6, 2015.
- [25] P. O. Box and C. Ch, “Shell Research Limited, Thornton Research Centre, P.O. Box 1, Chester CH1 3SH, England,” vol. 118, 1981.
- [26] E. Antolini, “Applied Catalysis B : Environmental Carbon supports for low-temperature fuel cell catalysts,” vol. 88, pp. 1–24, 2009.
- [27] S. Bong, Y. R. Kim, I. Kim, S. Woo, S. Uhm, J. Lee, and H. Kim, “Graphene supported 131, 2010. electrocatalysts for methanol oxidation,” *Electrochem. commun.*, vol. 12, no. 1, pp. 129–

# Chapter 2

## Literature Review

### 2.1 Role of Electro-catalysts

Success of DMFC to be competitive as viable energy source in the energy market depends upon the cost, efficiency and durability of the electro-catalyst. At present, most of the fuel cells (low temperature fuel cell) use Pt-based catalyst. Due to these expensive electro-catalyst manufacturing cost of the fuel cell is increased which greatly affects the successful commercialization. Beside these most of the Pt-based electro-catalyst face catalyst poisoning. Consequently, researchers are trying to develop a low cost, reliable and efficient electro-catalyst to replace Pt-base catalysts [1-3].

### 2.2 Electro-catalysis

So far significant numbers of studies have been performed by involving different techniques for the electro-oxidation of lower molecular weight organic compounds such as CO, CH<sub>3</sub>OH, HCOOH, and HCHO. Results from these investigations reveals that at low temperature electro-oxidation of these organic compounds need the presence of Pt-based catalyst. Two key steps dehydrogenation and chemisorption of CO are involved during the electro-oxidation of these compounds under Pt-based catalyst. A strongly adsorbed intermediate species (like CO, HCOOH) etc. are produced during all these reactions. These types of species (like CO) are adsorbed on the surface of the catalyst and cause for catalyst poisoning. The poisoning effect of the Pt catalyst significantly decreases power density and fuel consumption efficiency of the cell. To inhibit the poisoning effect and to increase the electro-oxidation rate by an order of three to four times a lot of research have been carried out to replace the Pt catalyst. Most suitable results have been achieved by alloying the Pt with Ru and Sn for the complete oxidation of methanol and CO. In recent years research is focused to develop non noble metal electro-catalysts such as Co, Ni, Pb, and W to replace platinum an expensive metal. However above transition metals show poor oxidation kinetics. By using high conductive material as a support like graphene, carbon nanotubes (CNTs) and carbon

Nano fibers electro-catalytic efficiency of these metals can be improved. Compared with other carbon support material graphene is an excellent electrode material because of its lower manufacturing cost, high surface area, and exceptional conductivity. Therefore, graphene can be used as catalytic support material to enhance the electrochemical activity of catalyst particle for methanol and ethanol oxidation [4-6].

### **2.3 DMFCs Catalyst Review**

Catalysts play a very crucial role in in the electro-oxidation of chemical fuel directly into electrical energy. So, for different catalyst has been prepared and used for the electro-oxidation of methanol since the discovery of direct methanol fuel cell. Platinum metals and alloys have been widely used as a sole catalyst and considered one of the most effective catalyst for the oxidation of methanol. Because of most expensive metal and other associated problems with platinum catalysts scientists and researchers are trying to develop new stable and cost-effective catalyst instead of Platinum catalysts.

#### **2.3.1 Platinum and Alloy catalysts**

Platinum is considered the most effective and suitable catalyst for methanol oxidation both in acidic and alkaline medium. Many researchers have addressed on the comparison and optimization of Pt and alloy catalysts under different conditions [7]. It has been observed that in case of Platinum ruthenium alloy catalyst, steady state MOR reaction has been obtained if atomic ratios of Pt/Ru were kept in range 9:1. Tripkovic et al reported that PtRu catalyst showed more activity towards methanol oxidation at room temperature as compared to alone Pt catalyst. Pt-Pd alloy catalysts using 15% Pd showed 10 times higher current densities in alkaline medium as compared to pure platinum [8-9]. So that Co- catalysts improves the atomic structure of Pt and reduces the catalyst poisoning from strongly adsorbed intermediate species on the catalysts surface. Comparing the binary Pt-based catalyst PtSn/C show more oxidation potential. PtRu binary and PtRuSn ternary catalysts showed tremendous results toward methanol oxidation [10].

### **2.3.2 Palladium and Alloy catalysts**

The introduction of alkaline medium was a great finding which was the main reason of using non-noble metal as catalyst for methanol oxidation. Because of which non-noble metals can survive longer time in the reaction medium as compared to the acidic medium. Naturally Pd exists 200 times more than Pt so Pd metal is available 30-40% lower prices. Moreover, Pd has proved superior catalyst for alcohol oxidation in alkaline medium than that of Pt. Furthermore, Pd alloy catalysts such as PdNi/C and PdSn/C are the most suitable catalyst for fuel cell application. Also, PdSn catalyst with carbon support has shown higher activity as compared to single Pd metal catalyst. Pd-NiO and Pt-NiO were also investigated for methanol oxidation Pd-NiO showed better response for methanol oxidation [11-13].

### **2.3.3 Non-noble metals Catalysts**

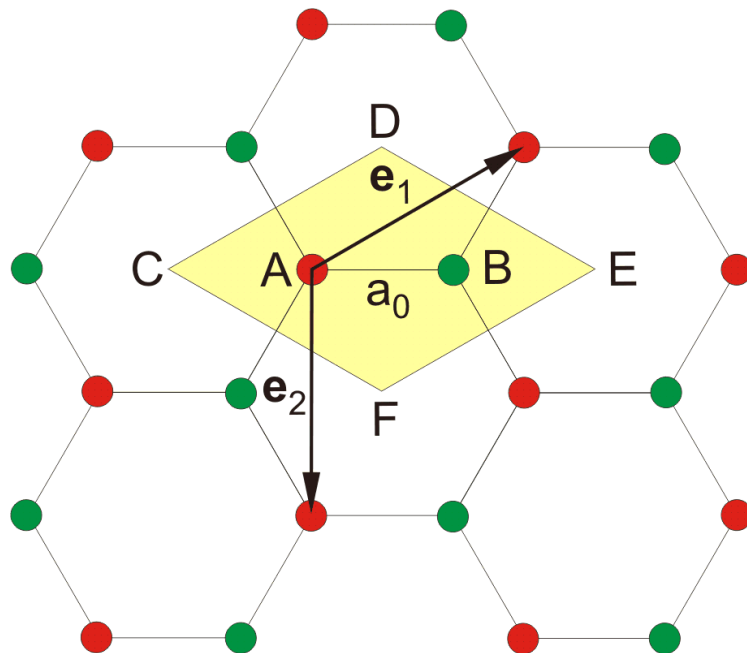
The great advantage of using alkaline environment for methanol oxidation is the opportunity of using non-precious metal catalyst. Among non-noble metals Ni is versatile material for its excellent properties of catalysis. It has been widely used as an electro-catalyst in many reactions such as organic synthesis and water electrolysis. During the last few decades it has been studied for the electro-oxidation of methanol. Roslonek et al reported that glassy carbon electrode modified with Ni(OH)<sub>2</sub> shows excellent activity towards methanol oxidation. Abdel Rahim et al studied the electrochemical properties of Ni for methanol oxidation by cyclic voltammetry technique [14]. They observed that Ni particles dispersed on graphite crystals show good oxidation towards methanol but massive amount of Ni does not show any response. Ni zeolite catalyst has been described as super effective catalyst for methanol oxidation as compared to Pt and Ni catalyst on graphite support. Shobba et al reported the synthesis of Co-W alloy by electroplating for methanol oxidation. Several researchers also reported the Lanthanum Strontium oxides. They studied the electro-oxidation of methanol on bulk and nano crystalline scale. LaSrCuO<sub>4</sub>, LaSrCuSbO<sub>4</sub>, LaSrCoO<sub>3</sub> were tested for methanol oxidation in 1M NaOH concentration. All above oxides showed reasonable currents for fuel cell applications [15-16].

## 2.4 Importance of Graphene and Graphene Oxide

Graphene is a wonder material due to its extraordinary physical, electrochemical, mechanical properties and potential for application in various fields of material science. Graphene contains large theoretical surface area approximately ( $3620 \text{ m}^2 \text{ g}^{-1}$ ), high electrical conductivity, high electron mobility ( $200,000 \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$ ), and good optical transmittance makes it a potential candidate for various applications such as conductive electrode material and many other applications. Graphite oxide is the potential source of the production of chemically modified graphene on a large scale. Graphene was first prepared about 150 years ago. Graphite oxide is the commercial source and precursor of large scale production of graphene based materials [17-18].

### 2.4.1 Properties of Graphene

Graphene is composed of a honeycomb lattice of carbon atoms bonded together with sigma bonds. Each carbon atom in the honeycomb lattice has a  $\pi$  orbital which shares the delocalized network of electrons. The microscopic study reveals that the lateral dimension is 8 to 10 nm and height is about 0.7 to 1 nm.



**Figure 2.1** Crystal structure of graphene [19]

Graphene owes superb electrical conductance properties at room temperature. It behaves like a zero-band gap semiconductor, charge carrier can be constantly tuned into electrons and holes in a very high concentration up to  $10^{13} \text{ cm}^{-2}$ , mobilities reaches up to  $150,000 \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$  at room temperature. By minimizing the impurity level exceptionally high level of mobilities can be achieved in suspended graphene up to  $200,000 \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$ . Due to low charge carrier densities, thermal conductivity of graphene (k) of graphene is negligible. It mainly depends upon the phonon transport, specifically diffusive conduction at very high temperature and ballistic conduction at very low temperature [20-21].

#### **2.4.2 Applications of Graphene**

Graphene is being used in various fields of science and technology such as field effect transistors. Transparent conductive films, sensors, supercapacitors, clean energy devices and graphene polymer nanocomposites. Graphene is considered excellent electrode material due its high theoretical surface area  $3620 \text{ m}^2 \text{ g}^{-1}$  and capability to support electron hole across its two-dimensional surface. Graphene has been recognized as catalyst support material in fuel cell for methanol oxidation and oxygen reduction. Graphene based materials are used as electrode material in dye sensitized solar cells. Graphene is a worthy substitute material of CNTs as catalyst support material [22-23].

#### **2.5 Graphene based Electro-catalysts**

Different types of carbon materials are commonly used as catalytic support electrode material in many applications of capacitors, batteries and fuel cells. Among them carbon nanotubes (CNTs) are more widely used because of tremendous electrical and structural properties Graphene is a 2 dimensional one atom thick layer of hexagonal  $\text{sp}^2$  carbon atoms. Due to its excellent physical and chemical properties has gain considerable scientific importance in the recent years. This wonder material has potential application in the field of batteries, super capacitors, sensors and especially as carbon support material in fuel cells. The development of very efficient electro-catalyst is extremely important for alternative sustainable energy harnessing technology including fuel cell. Graphene is becoming a unique material for its good electrical conductance and high surface area. Graphene based hybrid material based noble metals and non-noble metals electro-catalyst enhance the fuel oxidation and water splitting reactions [24-27].

## Summary

Electro-catalysts play very important role in the fuel cell operation. Without electro-catalysts redox reaction of the fuel cell is not possible. Commonly platinum and alloy catalysts are used at both anode and cathode in all low temperature fuel cells. So for different catalyst has been prepared and used for the electro-oxidation of methanol since the discovery of direct methanol fuel cell. Platinum is considered the most effective and suitable catalyst for methanol oxidation both in acidic and alkaline medium. Many researchers have addressed on the comparison and optimization of Pt and alloy catalysts under different conditions. The great advantage of using alkaline environment for methanol oxidation is the opportunity of using non-precious metal catalyst. Among non-noble metals Ni is versatile material for its excellent properties of catalysis. It has been widely used as an electro-catalyst many reactions such as organic synthesis and water electrolysis. The development of very efficient electro-catalyst is extremely important for alternative sustainable energy harnessing technology including fuel cell. Graphene is becoming a unique material for its good electrical conductance and high surface area. Graphene based hybrid material based noble metals and non-noble metals electro-catalysts enhance the fuel oxidation and water splitting reactions.

## References

- [1] 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.
- [2] Sun, Shuhui, et al. "Single-atom catalysis using Pt/graphene achieved through atomic layer deposition." *Scientific reports* 3 (2013).
- [3] Wang, Xiao, et al. "Green synthesis of Pt/CeO<sub>2</sub>/graphene hybrid nanomaterials with remarkably enhanced electrocatalytic properties." *Chemical Communications* 48.23 (2012): 2885-2887.
- [4] 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.
- [5] Li, Yongjie, et al. "Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation." *Carbon* 48.4 (2010): 1124-1130.
- [6] Dong, Lifeng, et al. "Graphene-supported platinum and platinum–ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation." *Carbon* 48.3 (2010): 781-787.
- [7] Gurau, Bogdan, et al. "Structural and electrochemical characterization of binary, ternary, and quaternary platinum alloy catalysts for methanol electro-oxidation 1." *The Journal of Physical Chemistry B* 102.49 (1998): 9997-10003.
- [8] Gasteiger, Hubert A., et al. "Methanol electrooxidation on well-characterized platinum-ruthenium bulk alloys." *The Journal of Physical Chemistry* 97.46 (1993): 12020-12029.
- [9] Radmilovic, V., H. A. Gasteiger, and P. N. Ross. "Structure and chemical composition of a supported Pt-Ru electrocatalyst for methanol oxidation." *Journal of Catalysis* 154.1 (1995): 98-106.



- [10] Wang, K., et al. "On the reaction pathway for methanol and carbon monoxide electrooxidation on Pt-Sn alloy versus Pt-Ru alloy surfaces." *Electrochimica Acta* 41.16 (1996): 2587-2593.
- [11] Cubeiro, M. L., and José Luis G. Fierro. "Partial oxidation of methanol over supported palladium catalysts." *Applied Catalysis A: General* 168.2 (1998): 307-322.
- [12] Pattabiraman, R. "Electrochemical investigations on carbon supported palladium catalysts." *Applied Catalysis A: General* 153.1-2 (1997): 9-20.
- [13] Li, Huanqiao, et al. "An improved palladium-based DMFCs cathode catalyst." *Chemical Communications* 23 (2004): 2776-2777.
- [14] Taraszewska, J., and G. Rosłonek. "Electrocatalytic oxidation of methanol on a glassy carbon electrode modified by nickel hydroxide formed by ex situ chemical precipitation." *Journal of Electroanalytical Chemistry* 364.1-2 (1994): 209-213.
- [15] Shobba, T., S. M. Mayanna, and C. A. C. Sequeira. "Preparation and characterization of Co–W alloys as anode materials for methanol fuel cells." *Journal of power sources* 108.1 (2002): 261-264.
- [16] Ramesh, L., B. S. Sheshadri, and S. M. Mayanna. "Electrolytic preparation and characterization of Ni–Fe–Mo alloys: cathode materials for alkaline water electrolysis." *International journal of energy research* 23.10 (1999): 919-924.
- [17] Zhu, Yanwu, et al. "Graphene and graphene oxide: synthesis, properties, and applications." *Advanced materials* 22.35 (2010): 3906-3924.
- [18] Chaudhuri, Biswadeep, et al. "Myoblast differentiation of human mesenchymal stem cells on graphene oxide and electrospun graphene oxide–polymer composite fibrous meshes: importance of graphene oxide conductivity and dielectric constant on their biocompatibility." *Biofabrication* 7.1 (2015): 015009.
- [19] Neto, AH Castro, et al. "The electronic properties of graphene." *Reviews of modern physics* 81.1 (2009): 109.

- [20] Balandin, Alexander A. "Thermal properties of graphene, carbon nanotubes and nanostructured carbon materials." *arXiv preprint arXiv:1106.3789* (2011).
- [21] Zhao, Xin, et al. "Enhanced mechanical properties of graphene-based poly (vinyl alcohol) composites." *Macromolecules* 43.5 (2010): 2357-2363.
- [22] Martins, T. B., et al. "Electronic and transport properties of boron-doped graphene nanoribbons." *Physical review letters* 98.19 (2007): 196803.
- [23] Wang, Caiyun, et al. "Electrochemical properties of graphene paper electrodes used in lithium batteries." *Chemistry of Materials* 21.13 (2009): 2604-2606.
- [24] Huang, Cancan, Chun Li, and Gaoquan Shi. "Graphene based catalysts." *Energy & Environmental Science* 5.10 (2012): 8848-8868.
- [25] Lai, Linfei, et al. "Exploration of the active center structure of nitrogen-doped graphene-based catalysts for oxygen reduction reaction." *Energy & Environmental Science* 5.7 (2012): 7936-7942.
- [26] Huang, Xiao, et al. "Graphene-based composites." *Chemical Society Reviews* 41.2 (2012): 666-686.
- [27] Mungse, Harshal P., et al. "Grafting of oxo-vanadium Schiff base on graphene nanosheets and its catalytic activity for the oxidation of alcohols." *Journal of materials chemistry* 22.12 (2012): 5427-5433.

# Chapter 3

## Synthesis Methods and Characterization Techniques

### 3.1 Graphene Nano-composites Synthesis Methods

Recently, various methods have been adopted for the synthesis of graphene based nano-composites material. Following are some important electro-catalyst preparation methods for low temperature fuel cell.

#### 3.1.1 Physical Synthesis Methods

Physical methods usually involve the use of heat energy in the form electricity or light for the evaporation of material in vacuum or inert atmosphere and to deposit gaseous atoms to form nano scale material. Some of the well-known reported method includes.

- (i) Molecular Beam Epitaxy (MBE)
- (ii) Thermal evaporation method
- (iii) Spray coating technology

Molecular beam epitaxy is the method to develop thin film of different compounds by the help of crystal substrate. Various materials are heated in a furnace under high vacuum and vapor are generated and sprayed from a small hole directly on the substrate. By controlling the molecular beam and substrate atoms are arranged in layer in multiple layers. However, MBE is very costly and complicated process because high degree of vacuum and controlling the molecular beam is a challenging job [1-3].

### 3.2 Chemical Synthesis Methods

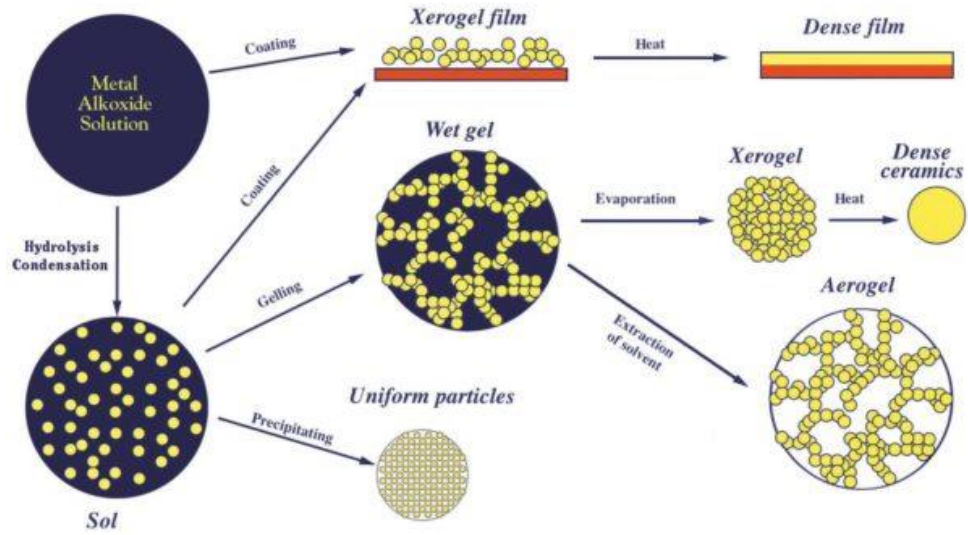
Chemical synthesis methods include chemical reduction method, sol gel method, electrochemical deposition and hydrothermal method. Let us explain some of these methods

#### 3.2.1 Chemical Reduction Process

Chemical reduction is the famous method for the preparation of nano-material. In chemical reduction method first of all aqueous solution of metal precursor of the catalyst material is made through vigorous stirring process. Then some reducing agent is added in the aqueous phase. With the help of reducing agents ionic compounds are reduced to metal nano-composites. Ethylene glycol, sodium borohydride and hydrazine hydrate are some commonly used reducing agents in the chemical reduction process. The chemical reduction is a low cost and easy method for the mass production of nano-composites catalyst. However, reducing agent and other organic solvents can affect the binding strength of nano-composites and performance might be reduced [4-5].

### **3.2.2 Sol-gel Method**

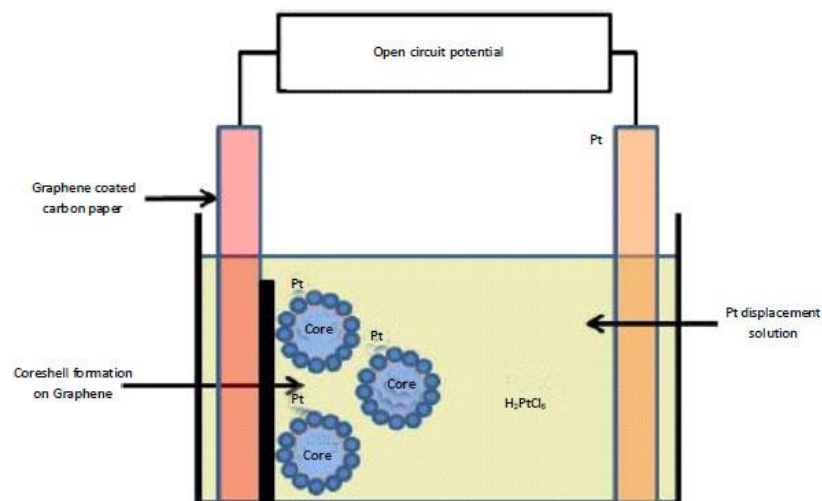
In sol-gel method metal chlorides and metal alkoxides are used as metal precursors. These metal chloride and oxides are treated with series of hydrolysis and condensation process. The prepared material is then dried in vacuum drier at specific temperature. Finally, after calcination the require nano-composites catalyst is obtained. Sol gel is considered very effective process for the synthesis of thin-film coated material. This is a low temperature method and easy to handle, but there are some bewildering factors which still exists in the process of sol formation [6-7].



**Figure 3.1** Schematic diagram of sol gel method

### 3.2.3 Electrochemical Deposition

Electrochemical deposition method of nano-composites synthesis is a well-established method and has gain industrial importance. The electro deposition is done in electrochemical cell. The catalytic precursor solution is used as electrolyte which is deposited at electrode made up of some substrate material by passing electrical current. The uniform electrochemical deposition of nano particles is controlled by controlling the amount of electric current and the reaction time. The electrochemical method has many advantages such as controlled deposition, easy operation and environment friendly in nature. However, in case of graphene based metal nano-composites the metal practical may not be penetrate deep into the graphene sheets, but only deposit on the upper surface of the graphene and thus make the unreliable binding. Regarding this draw back this method still need further investigation of binding strength [8].



**Figure 3.2** Schematic diagram of electrochemical deposition method [9]

### 3.2.4 Hydrothermal method

The main difference between hydrothermal and sol gel method is the temperature and vapor pressure. Hydrothermal method works in temperature range 130 °C to 250 °C and vapor pressure is about 0.3 to 4 MPa. In hydrothermal method nanocomposites are synthesis by simply generation of high vapor pressure at constant volume and high temperature. Most of the reactants are completely dissolved into the water which act as reaction media. Homogenous mixing of the reactants speeds up the reaction rate. Hydrothermal method has following advantages for the synthesis of graphene nano-composites.

- 1) Good crystalline structure
- 2) Narrow particle size and less agglomeration
- 3) More purity and excellent morphology

Hydrothermal method has great potential of further development because electro-catalysts synthesized by this method show excellent electrochemical activity [10-11].

### 3.3 Characterization Techniques

In our present work different characterization techniques have been used to identify the structure and morphology of the prepared electro-catalyst nano-composites material like X-ray diffraction, scanning electron microscopy, and particle size analyzer.

### 3.3.1 X-ray diffraction (XRD)

In 1896, a German scientist Wilhelm Rontgen discovered the X-rays. Later on, in 1913 W.L. Bragg used these electromagnetic radiations for the structural identification of the crystalline material. XRD is non-destructive analytical tool for the identification of phase and orientation of the crystalline compounds. It is useful technique to determine the structural properties, lattice parameters and crystalline size.

#### Working principle of XRD

When a plane of crystalline material is irradiated by a beam of X-ray they are refracted back by the atoms of the material at certain angle. A unique pattern is created by each material. An independent pattern is generated by each substance in a mixture of multiple materials. When X-rays interact with atoms of certain material electrons in atom start vibrating with the same striking frequency of the X-rays. This phenomenon can be explained with the help of Bragg's law as shown in the equation (3.1)

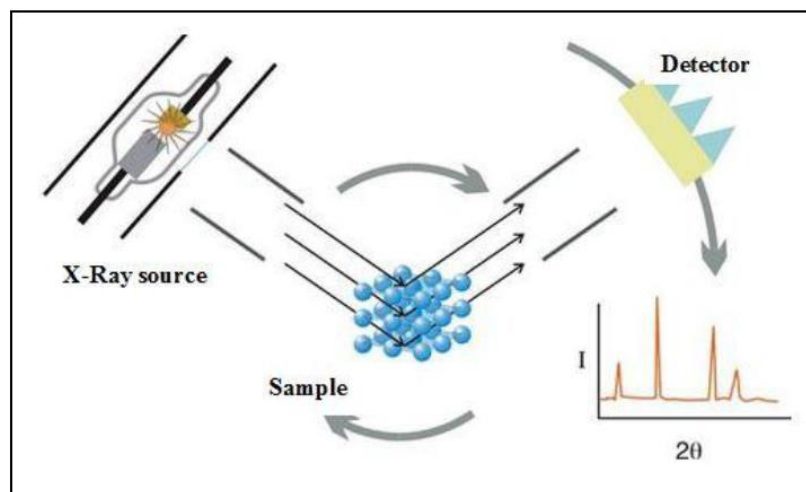
$$n\lambda = 2d\sin\theta \quad (3.1)$$

Where:

$\lambda$  = wave length of the X-rays

$\theta$  = incident angle

d = spacing between crystal planes



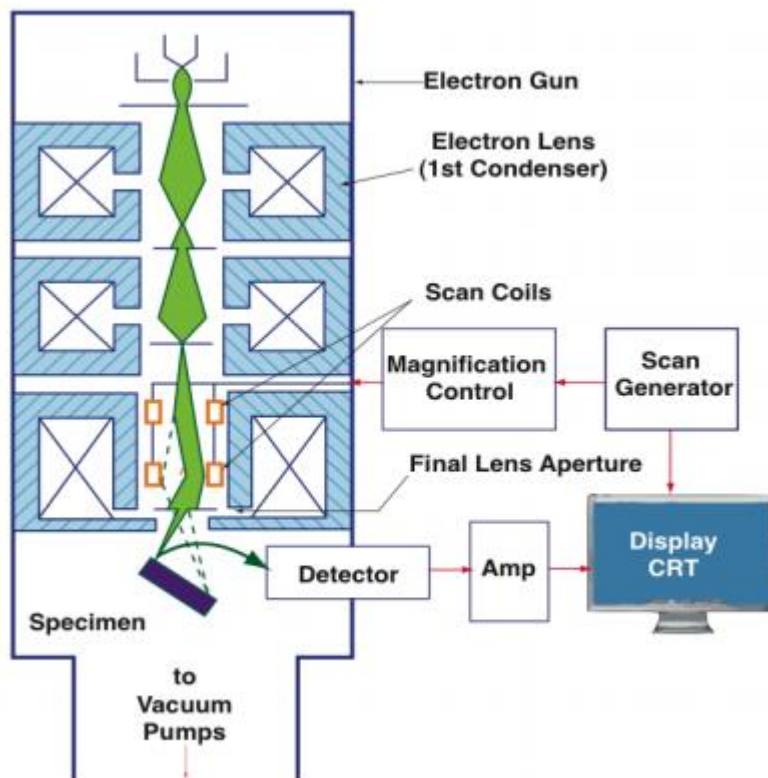
**Figure 3.3** Working mechanism of XRD

Figure shows the working mechanism of XRD machine. A beam of X-ray is generated from the X-ray generator which strikes on the sample material at a certain angle. After striking with the sample material X-rays are detected by the detector which makes the diffractogram. A diffractogram is a graphical pattern which is plotted between  $2\theta$  on x-axis and intensity on y-axis. The detector records the intensities of the diffracted beams and angles. The pattern obtained is almost the finger print of the material. Each material has its own unique finger print. Miller indices define the inter-planer spacing and orientation. Number and position of the peaks ( $2\theta$ ) values enable to determine lattice type, cell parameter and crystal structure. Intensity of peaks gives information about the position and types of the atoms in a specimen [12-14].

### 3.3.2 Scanning electron microscopy (SEM)

SEM is a very useful imaging tool which is used to investigate the surface morphology of the sample. It gives the three-dimensional image of specimen surface with resolution and magnification. SEM can provide 300,000 X stronger magnification with effective depth of 1  $\mu\text{m}$  to 10 nm.





**Figure 3.4** Schematic diagram of SEM working mechanism

### **Working principle**

A typical SEM setup consists of electron gun, scanning system, detector and display. An electron beam of spot size less than 10 nm in diameter is generated by the electron gun. In order to generate an image electron beam is focused on the specimen. When any portion of the specimen is struck by highly accelerated electron emits signal in the form of electromagnetic radiation. Selected portion of these backscattered radiations is collected at the detector. This signal is amplified and displayed on TV screen in the form of image. The magnification depends on the relationship of size between the display and area of the surface being scanned. Samples under scanned by SEM may face damage problem but rarely happens [15-17].

### **3.4 Particle size analyzer**

Particle size analyzer is tool to identify the range of particles sizes present in the samples. This technique also gives information about average particle size along with the percentage of particular sizes formed in the powder samples

### **Working principle**

Particle size analyzer consists of two chambers first chamber is a conical type that is connected to an electric motor and second chamber is transparent box. Powder sample is sonicated before feeding the liquid suspension of powder sample into the conical chamber. After inserting the sample into the conical section, the suspension is mixed again with motor and then it goes to transparent section. Here the particles are suspended and laser beam is passed through the transparent section and strikes the particles. A detector is placed on the other side of the laser source that measures the particles present in the samples [18-19].

### **3.5 Energy dispersive X-ray spectroscopy (EDX analysis)**

Energy dispersive X-ray spectroscopy is an analytical technique which is used for the determination of element present in the given sample. It also gives information about the chemical characterization of the samples

#### **Working principle**

The fundamental principle of energy dispersive X-ray spectroscopy is that each element present in a sample emits unique set of electromagnetic radiation when excited by highly active and focused beam of electron [20-21].

### **3.6 Electrochemical measurement techniques**

In our present work, the electrochemical reactivity of the synthesized electrocatalyst was analyzed by cyclic voltammetry technique

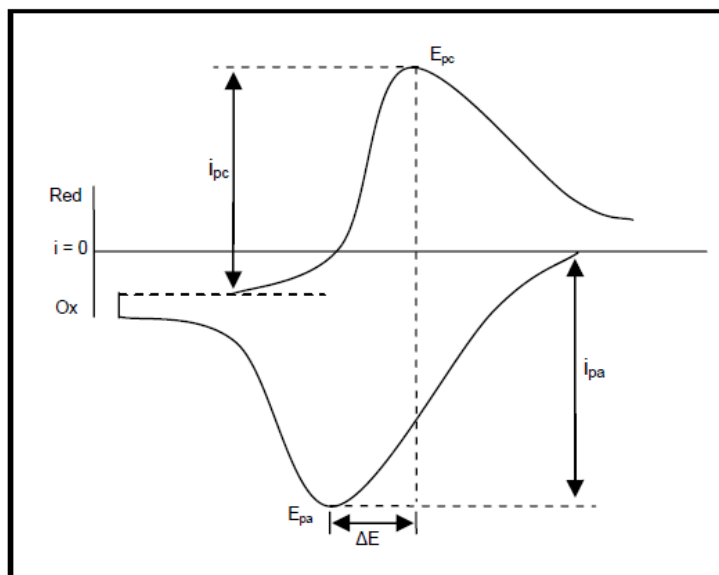
#### **3.6.1 Cyclic voltammetry (CV)**

Cyclic voltammetry is the common electrochemical reactivity measurement technique. CV measures the intensity of current produced during electrochemical reaction against the potential applied on the working electrode.

- **Working principle**

In a typical CV experiment, a potential is applied by the potentiostat on the working electrode in a complete cycle. The potential is gradually increased then the scan reverses

and returns to the starting position. Potentiostat measures the resulting current produced during a potential sweep against the applied potential. A theoretical cyclic voltammogram for a typical experiment is shown in the Fig. 3.5



**Figure 3.5** Typical CV curve

In a typical CV experiment, a potential is applied by the potentiostat on the working electrode in a complete cycle. The potential is gradually increased then the scan reverses and returns to the starting position. Potentiostat measures the resulting current produced during a potential sweep against the applied potential. A graph is plot from these current values against the applied potential called the CV graph or CV plot. In a typical CV experiment the result obtained depends on various factors. In a series of experiment different parameters are selectively varied like the applied potential, scan rate, molar concentration of the supporting electrolyte and species concentration of the working electrolyte [22-25].

## **Summary**

Different types of methods have been used for the syntheses of graphene oxide but Modified Hummer's method and Improve Hummer's methods are most suitable methods for the synthesis of graphene oxide. Recently, various methods have been adopted for the synthesis of graphene based nano- composites material. Chemical reduction is the famous method for the preparation of nano material. For the identification successful synthesis nanocomposites XRD, SEM and particle size analysis were used. XRD gives information about the structure, phase and crystalline structure of the given sample. Whereas SEM is used to identify the surface morphology of samples. For the elemental analysis of the prepared material EDX technique was used. Particle size of the synthesized material was measure by particle size analyzer. Electrochemical properties of the synthesized nanocomposites catalysts were investigated by cyclic voltammetry.

## References

- [1] Ruiz, Ruiz de Gopegui. "Molecular beam epitaxy, MBE." *Revista Espanola de Fisica* 24.2 (2010): 41-46.
- [2] Mahmoud, S. A., A. A. Ibrahim, and A. S. Riad. "Physical properties of thermal coating CdS thin films using a modified evaporation source." *Thin Solid Films* 372.1 (2000): 144-148.
- [3] Lee, Chang-Hee. "Spray Coating Technology." *Journal of ILASS-Korea* 13.4 (2008): 193-199.
- [4] Stankovich, Sasha, et al. "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide." *carbon* 45.7 (2007): 1558-1565.
- [5] Guzmán, Maribel G., Jean Dille, and Stephan Godet. "Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity." *World Academy of Science, Engineering and Technology* 43 (2008): 357-364.
- [6] Antonelli, David M., and Jackie Y. Ying. "Synthesis of hexagonally packed mesoporous TiO<sub>2</sub> by a modified sol-gel method." *Angewandte Chemie International Edition* 34.18 (1995): 2014-2017.
- [7] Chen, Dong-Hwang, and Xin-Rong He. "Synthesis of nickel ferrite nanoparticles by sol-gel method." *Materials Research Bulletin* 36.7 (2001): 1369-1377.
- [8] Paunovic, Milan, and Mordechai Schlesinger. *Fundamentals of electrochemical deposition*. Vol. 45. John Wiley & Sons, 2006.
- [9] Shin, H-C., Jian Dong, and Meilin Liu. "Nanoporous structures prepared by an electrochemical deposition process." *Advanced Materials* 15.19 (2003): 1610-1614.
- [10] Rabenau, Albrecht. "The role of hydrothermal synthesis in preparative chemistry." *Angewandte Chemie International Edition* 24.12 (1985): 1026-1040.
- [11] Yaghi, O. M., and Hailian Li. "Hydrothermal synthesis of a metal-organic framework containing large rectangular channels." *Journal of the American Chemical Society* 117.41 (1995): 10401-10402.

- [12] Whittig, L. D., and W. R. Allardice. "X-ray diffraction techniques." *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods* methodsofsoilan1 (1986): 331-362.
- [13] Whittig, L. D., and W. R. Allardice. "X-ray diffraction techniques." *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods* methodsofsoilan1 (1986): 331-362.
- [14] Brown, G. T., and G. W. Brindley. "X-ray diffraction procedures for clay mineral identification." *Crystal structures of clay minerals and their X-ray identification 5* (1980): 305-359.
- [15] Michler, Goerg H. "Scanning electron microscopy (SEM)." (2008): 87-120.
- [16] Goldstein, Joseph, et al. *Scanning electron microscopy and X-ray microanalysis: a text for biologists, materials scientists, and geologists*. Springer Science & Business Media, 2012.
- [17] Cimmino, S., E. Martuscelli, and C. Silvestre. "Scanning Electron Microscopy (SEM)." *Test Procedures for the Blood Compatibility of Biomaterials*. Springer Netherlands, 1993. 211-228.
- [18] Erdmann, Joachim C., Robert I. Gellert, and Richard L. Skaugset. "Particle size analyzer." U.S. Patent No. 4,179,218. 18 Dec. 1979.
- [19] Pogue, Glenn J., and William E. Lower. "Particle size analyzer." U.S. Patent No. D294,948. 29 Mar. 1988.
- [20] Meher, Ashutosh, and Amiya Ranjan Pradhan. "Energy Dispersive X-ray Spectroscopy (EDX) analysis of *Curculigo orchioides* Gaertn. root tubers." *Drug Invention Today* 2.1 (2010).
- [21] Mishra, Ashutosh, et al. "Energy Dispersive X-Ray Spectroscopy (EDX) Analysis of *Ichnocarpus frutescens* Plant Parts." *Drug Invention Today* 1.1 (2009).
- [22] Kissinger, Peter T., and William R. Heineman. "Cyclic voltammetry." *J. Chem. Educ* 60.9 (1983): 702.

[23] Mabbott, Gary A. "An introduction to cyclic voltammetry." *J. Chem. Educ* 60.9 (1983): 697.

[24] Van Benschoten, James J., et al. "Cyclic voltammetry experiment." *J. Chem. Educ* 60.9 (1983): 772.

[25] Evans, Dennis H., et al. "Cyclic voltammetry." (1983): 290.

# Chapter 4

## Experimentations

### 4.1 Preparation of Graphene Oxide (GO)

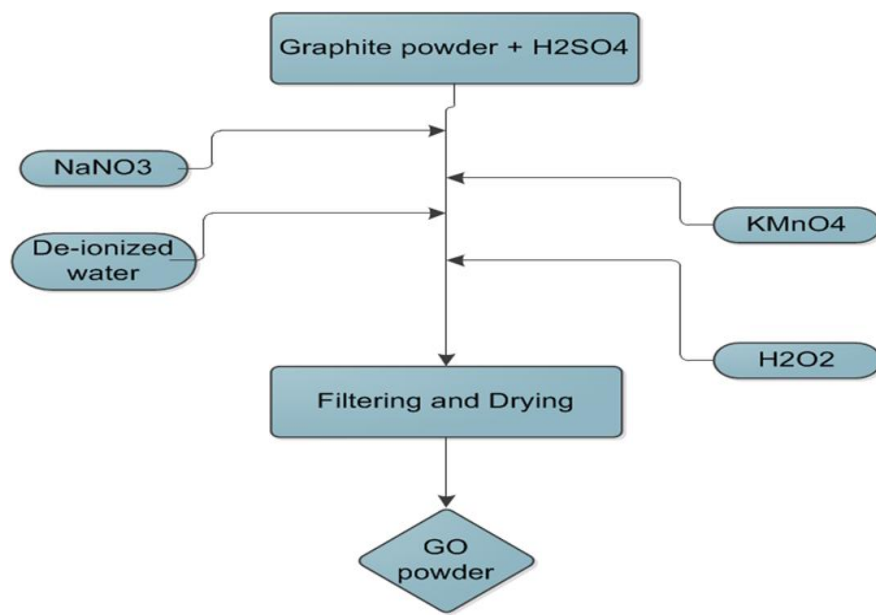
#### 4.1.1 Materials and Reagents

Graphite Powder (99.99%) of particle size 45  $\mu\text{m}$ ,  $\text{H}_2\text{SO}_4$  (98%),  $\text{NaNO}_3$  (99%),  $\text{KMnO}_4$  (99%),  $\text{H}_2\text{O}_2$  (30%) were purchased from Sigma Aldrich (USA). All the reagents were of analytical grades and used without further purification.

#### 4.1.2 Chemical Procedure

Graphene oxide (GO) is synthesized from graphite powder by modified Hummer's method [1-2]. In the typical procedure 1g of graphite powder was mixed with 25 ml 98 % sulphuric acid ( $\text{H}_2\text{SO}_4$ ), and 1 g of sodium nitrate ( $\text{NaNO}_3$ ) taken in an ice bath for three hours followed with the addition of 5 g of potassium permanganate. The reaction was kept under vigorous stirring at 30  $^\circ\text{C}$ . Then slow addition of 100 ml water is performed. After this the obtained product was placed at 85 $^\circ\text{C}$  for two hours, then reaction was treated with 10 ml hydrogen peroxide ( $\text{H}_2\text{O}_2$  35 %). Finally, the obtained yellowish cake was centrifuged in order to get pure product where solution was washed several times with distilled water and ethanol.





**Figure 4.1** Typical flow chart of modified Hummer's method of graphene Oxide synthesis

## 4.2 Preparation of Ni/Co Graphene Nano-composites

### 4.2.1 Materials and Reagents

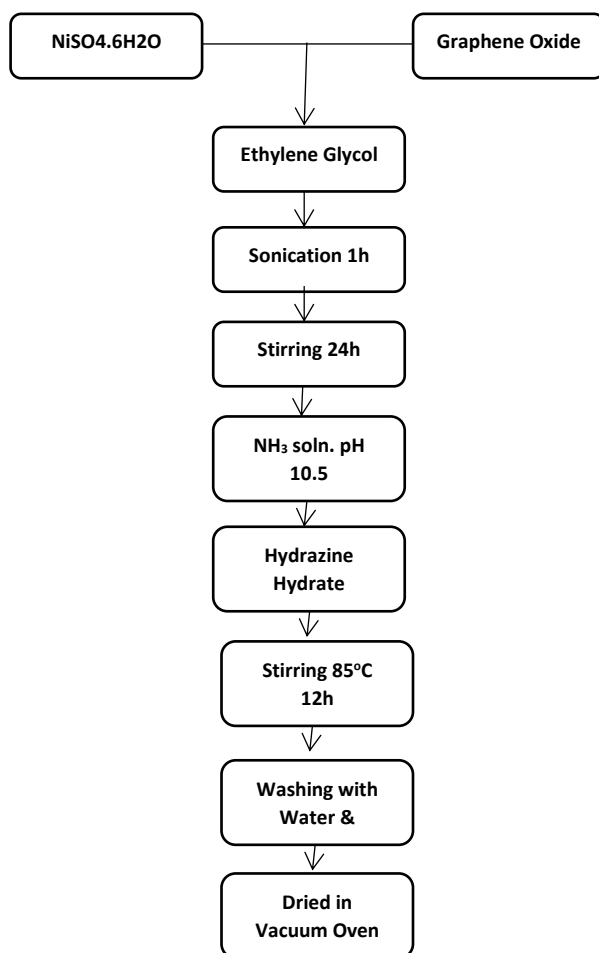
GO which was already prepared from modified Hummer's method.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Ethylene Glycol, and  $\text{NH}_3$ . All these reagents were purchased from Sigma-Aldrich (USA) of analytical grades and used without further cleaning and purification

### 4.3 Chemical Procedure

#### 4.3.1 Synthesis of Ni/graphene nanocomposites

In the present work deposition of nickel nanoparticles on graphene was obtained by using simple solution synthesis method. In this method, we have used ethylene glycol as a solvent and hydrazine hydrate as a reducing agent. In the typical procedure, 262.8 mg of nickel sulfate hexa-hydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), and 100 mg of graphene oxide (GO) that we have synthesized from graphite powder by a modified Hummer's method, nickel precursor and graphene oxide were added in a 100-ml flask having 60 ml ethylene glycol that was used as a solvent. After this the mixture was ultrasonicated for an hour,

then stirring is performed for 24 hours at ambient temperature. Then ammonia solution is added into the obtained mixture with stirring in order to obtain pH 10.5. After that 1 ml of hydrazine hydrate was added as a reducing agent into the above solution and the reduction reaction was performed under constant stirring at 85°C for 12 hours. The obtained product is then centrifuged in order to get pure product, washing is performed various times with distilled water and ethanol and dried in a vacuum desiccator at room temperature [3-5].

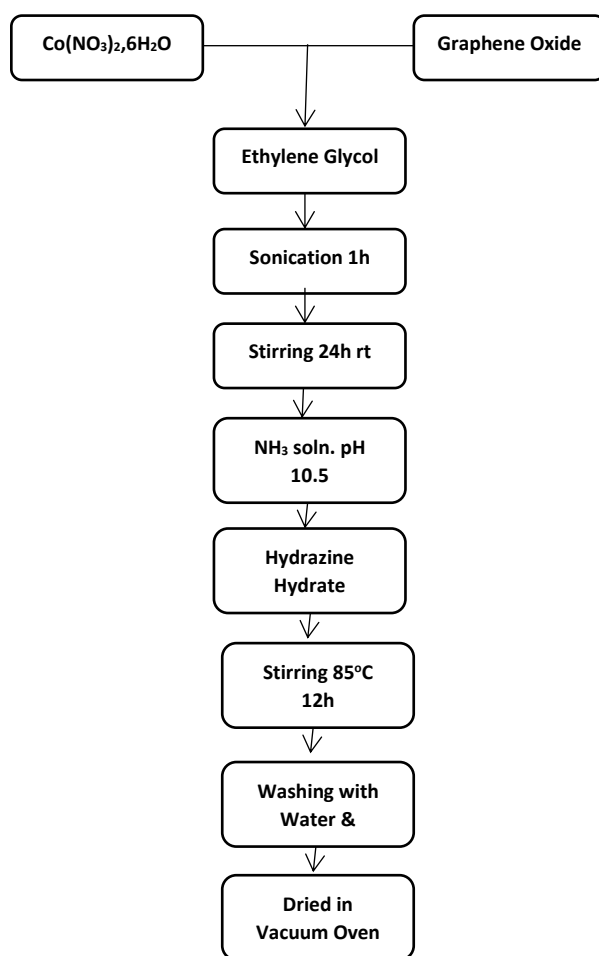


**Figure 4.2** Figurative flow chart of Ni-G nanocomposites synthesis

#### 4.3.2 Synthesis of Co/graphene nanocomposites

Similarly, deposition of cobalt nanoparticles on graphene was done by using simple solution synthesis method. In this method, we have used ethylene glycol as a solvent and

hydrazine hydrate as a reducing agent. In the typical procedure, 290 mg of cobalt nitrate hexa-hydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and 100 mg of graphene oxide (GO) that we have synthesized from graphite powder by a modified Hummer's method, cobalt precursor and graphene oxide were added in a 100-ml flask having 60 ml ethylene glycol that was used as a solvent. After this the mixture was ultrasonicated for an hour, then stirring is performed for 24 hours at ambient temperature. Then ammonia solution is added into the obtained mixture with stirring in order to obtain pH 10.5. After that 1ml of hydrazine hydrate was added as a reducing agent into the above solution and the reduction reaction was performed under constant stirring at  $85^\circ\text{C}$  for 12 hours. The obtained product is then centrifuged in order to get pure product, washing is performed various times with distilled water and ethanol and dried in a vacuum desiccator at room temperature [6-8].



**Figure 4.3** Figurative flow chart of Co-G nanocomposites synthesis

In order to investigate the phase, crystal structure and lattice parameter of the prepared nanocomposites, X-ray powder diffractometer (STOE Germany) with computer interface was used having radiation source Cu K $\alpha$  at  $\lambda = 1.5418 \text{ \AA}$ . The scan angle  $2\theta$  was selected  $0^\circ$ - $80^\circ$  with step size 0.04/sec.

To study the surface morphology of the synthesized catalyst scanning electron microscope (HITACHI SU- 1500) with 50  $\mu\text{m}$  magnification and voltage was kept up-to 5 kV

#### 4.4 Electrochemical Measurement Technique

All the electrochemical measurements were performed by using AUTOLAB 4.9 Potentiostat connected to PC. We used Ag/AgCl electrode as reference electrode in this work. The counter electrode was a Pt wire 1 mm thick and 12 cm long. 1M KOH solution was used as supporting electrolyte with 3M methanol concentration in a conventional three-electrode Pyrex glass electrochemical cell. The electrochemical characterization of the prepared Ni/graphene and Co/graphene nano-composites was done by using cyclic voltammetry technique



**Figure 4.4** Conventional three electrode Pyrex glass cell

- **Preparation of supporting electrolyte solution 1M KOH solution**

For the preparation of 50 ml supporting electrolyte 1M KOH solution, 20 g of solid KOH pellets were dissolved in 50 ml of water in 50 ml flask at ambient temperature

- **Preparation of 3 molar methanol solution with 1MKOH**

For the preparation of 50 ml 3 molar methanol solution, 3 ml of methanol was dissolved in 50 ml volume flask containing already 1M KOH solution at ambient temperature.

- **Preparation of functional material slurry**

For the modification of working electrode a homogenous slurry of the functional material was prepared by mixing 2 mg fine powder of the active material (Ni/graphene and Co/graphene), 20 $\mu$ l of nafion solution and 400 $\mu$ l of isopropanol in a small glass beaker. After sonicating the slurry for 30 min at room temperature, 15 $\mu$ l from the prepared slurry was poured on the active surface of the glassy carbon electrode which was then air dried at room temperature.



**Figure 4.5** Typical Glassy carbon electrode and Nafion solution

- **Preparation of working electrode (Platinum electrode)**

In the present work, platinum electrode with 2 mm in diameter was modified as working electrode. The working electrode was first washed and cleaned with distilled water then polished with alumina slurry. For the modification of working electrode, homogenous slurry of the functional material was prepared by mixing 2 mg fine powder of the active material, 20 $\mu$ l of nafion solution and 400 $\mu$ l of isopropanol. After sonicating the slurry for 30 minute at room temperature, 15 $\mu$ l from the prepared slurry was poured on the active surface of the platinum electrode which was then air dried at room temperature.



**Figure 4.6** Typical 2mm Platinum electrode

- **Preparation of working electrode (Glassy Carbon electrode)**

In the present work, glassy carbon electrode with active area 0.071 cm<sup>2</sup> was modified as working electrode. The working electrode was first washed and cleaned with distilled water than polished with alumina slurry. For the modification of working electrode a homogenous slurry of the functional material was prepared by mixing 2 mg fine powder of the active material, 20 $\mu$ l of nafion solution and 400 $\mu$ l of isopropanol. After sonicating the slurry for 30 min at room temperature, 15 $\mu$ l from the prepared slurry was poured on the active surface of the glassy carbon electrode which was then air dried at room temperature. The obtained current densities were normalized based on the utilized

surface area of the modified glassy carbon electrode. The response of peak current was checked at various scan rates ranging from  $25\text{mVs}^{-1}$  to  $100\text{mVs}^{-1}$  at starting potential starting from 0 mV to 1800 mV positive vertex potential.



**Figure 4.7** Modified Glassy carbon electrode

## 4.5 Cyclic Voltammetry

In order to investigate electrochemical behavior of prepared Ni/ graphene and Co/graphene nanocomposites cyclic voltammogram was recorded on both modified platinum electrode and modified glassy carbon electrode as a working electrode. The cyclic voltammogram (CVs) of Ni/graphene and Co/graphene nano-composites for methanol oxidation was done in alkaline medium. For the comparison cyclic voltammogram of bare GCE, Ni/ graphene and Co/graphene were recorded under same conditions at a scan rate of  $100\text{mVs}^{-1}$ , 1M KOH and 3M methanol concentration.

The anodic peak current observed for the period of forward scan was due to the electro-oxidation of methanol into intermediate species and further complete oxidation of these species into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and electrons. During the reverse scan, oxidation peak is obtained due to the remaining species that was not fully oxidized during the forward scan [9-11].



**Figure 4.8** AUTOLAB 4.9 Potentiostat setup



## **Summary**

Graphene oxide was synthesized by modified Hummer's method. Co/graphene and Ni/graphene nanocomposites were synthesis by chemical reduction method with the help of reducing agent. In our present work we synthesized Ni/graphene and Co/graphene nanocomposites by a facile, economic and environmental friendly method. Furthermore, the synthesized materials were characterized by XRD, SEM and EDX. The electrochemical activity of the synthesized electrocatalysts towards methanol oxidation was characterized by using cyclic voltammetry technique.

## References

- [1] Dreyer, Daniel R., et al. "The chemistry of graphene oxide." *Chemical Society Reviews* 39.1 (2010): 228-240.
- [2] Chen, T., et al. "High throughput exfoliation of graphene oxide from expanded graphite with assistance of strong oxidant in modified Hummers method." *Journal of Physics: Conference Series*. Vol. 188. No. 1. IOP Publishing, 2009.
- [3] Cao, Yu, et al. "One-step chemical vapor synthesis of Ni/graphene nanocomposites with excellent electromagnetic and electrocatalytic properties." *Synthetic Metals* 162.11 (2012): 968-973.
- [4] Liu, Minmin, Ruizhong Zhang, and Wei Chen. "Graphene-supported nanoelectrocatalysts for fuel cells: synthesis, properties, and applications." *Chemical reviews* 114.10 (2014): 5117-5160.
- [5] 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.
- [6] Zheng, Y. X. "Electrooxidation of propanol at the nano Ni-B amorphous alloy powder micro electrode." *J Huaqiao Univ Nat Sci* 31 (2010): 422-425.
- [7] Barakat, Nasser AM, et al. "Ni x Co 1- x alloy nanoparticle-doped carbon nanofibers as effective non-precious catalyst for ethanol oxidation." *International Journal of Hydrogen Energy* 39.1 (2014): 305-316.
- [8] Xu, Wei, et al. "Nickel-cobalt bimetallic anode catalysts for direct urea fuel cell." *Scientific reports* 4 (2014): 5863.
- [9] Hofstead-Duffy, Augusta M., et al. "Origin of the current peak of negative scan in the cyclic voltammetry of methanol electro-oxidation on Pt-based electrocatalysts: a revisit to the current ratio criterion." *Journal of Materials Chemistry* 22.11 (2012): 5205-5208.

[10] Barakat, Nasser AM, and Moaded 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] Barakat, Nasser AM, et al. "Carbon nanofibers doped by Ni x Co 1- x alloy nanoparticles as effective and stable non precious electrocatalyst for methanol oxidation in alkaline media." *Journal of Molecular Catalysis A: Chemical* 394 (2014): 177-187.

# Chapter 5

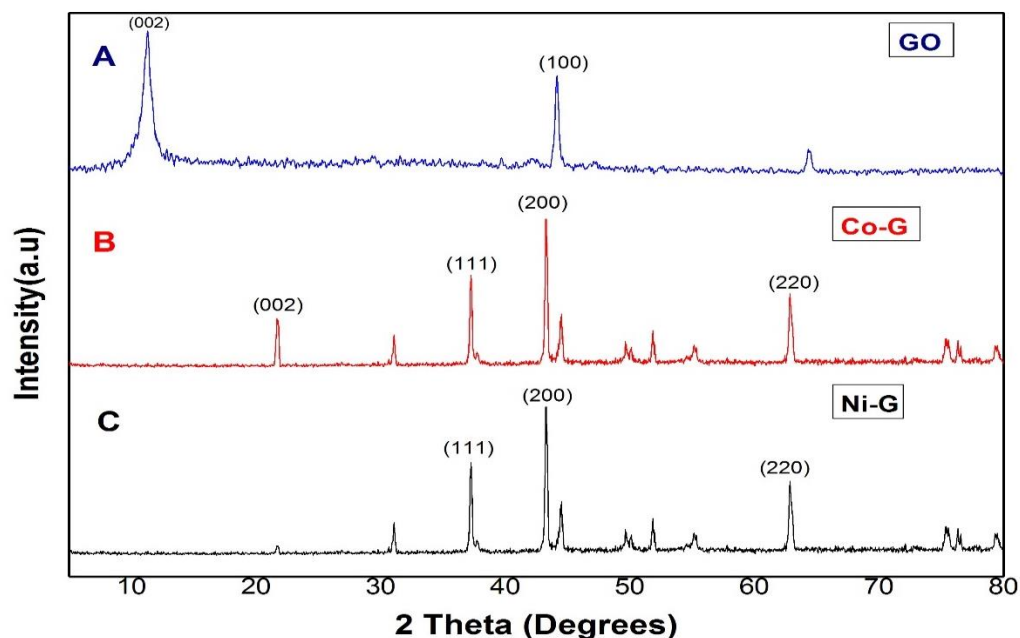
## Result and Discussions

### 5.1 Characterization Techniques

#### 5.1.1 X-ray Diffraction (XRD)

In order to investigate the phase, crystal structure and lattice parameter of the prepared nanocomposites, X-ray powder diffractometer (STOE Germany) with computer interface was used having radiation source Cu K $\alpha$  at  $\lambda = 1.5418 \text{ \AA}$ . The scan angle  $2\theta$  was selected  $0^\circ$ - $80^\circ$  with step size  $0.04/\text{sec}$ .

To investigate the successful synthesis of nano-composites characterization was done by performing X- ray diffraction and scanning electron microscopy. XRD pattern of graphene oxide (GO) is shown in the figure 5.1(a). The characteristic peak is obtained at  $2\theta$  of  $11.5^\circ$  clearly indicates the synthesis of graphene oxide, which shows that effective oxidation of graphite leads to the formation of graphene oxide. The XRD pattern of prepared Co/graphene nanocomposites is shown in the figure 5.1. (b) The typical reflection peak at  $2\theta = 22.3^\circ$  indicates the formation of graphene by the reduction process of graphene oxide. On the other hand, the diffraction bands obtained at  $2\theta = 37.4^\circ, 44.3^\circ$  and  $63.2^\circ, 62.1^\circ$  can be assigned to the characteristic of face center cubic (fcc) structure of Co nanoparticles.



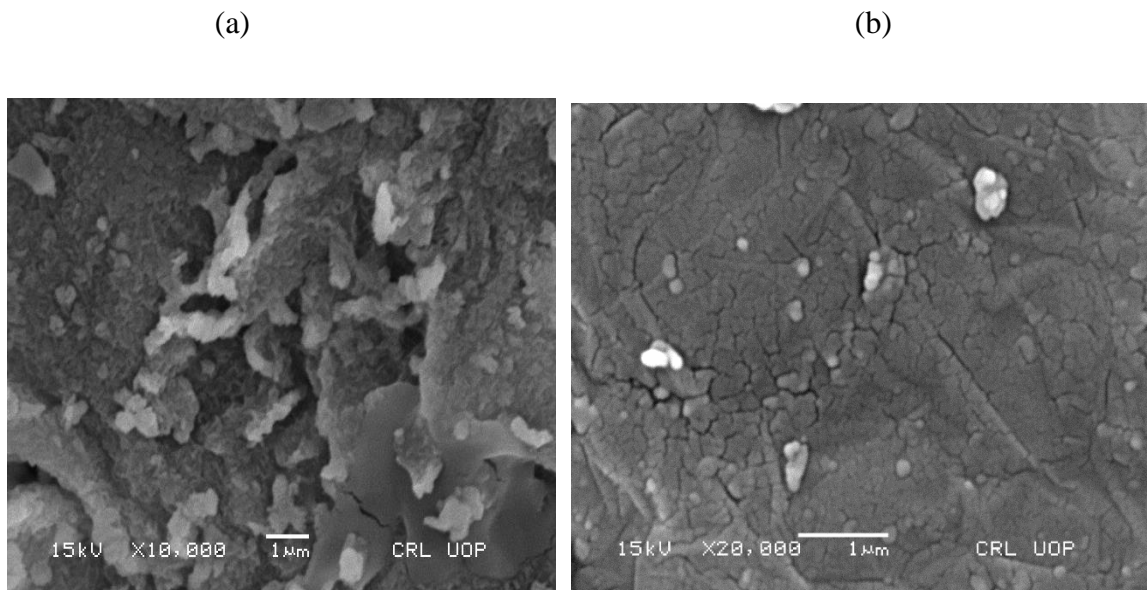
**Figure 5.1** (a) XRD pattern of GO (b) XRD pattern of Co-G (c) XRD pattern of Ni-G

The XRD display of Ni/graphene nanocomposites is shown in the figure 5.1(c). The typical reflection peak at  $2\theta = 22.3^\circ$  indicates the formation of graphene which was obtained by the reduction process of graphene oxide. On the other hand, the diffraction bands obtained at  $2\theta = 37.4^\circ$ ,  $44.3^\circ$  and  $63.2^\circ$ , can be assigned to the characteristic of face center cubic (fcc) structure of Ni nanoparticles. Cobalt and Nickel have almost similar crystal structure under normal conditions due to closer atomic numbers and molecular weights. That is the reason XRD patterns of Ni and Co are almost similar [1-2].

### 5.1.2 Scanning Electron Microscopy (SEM)

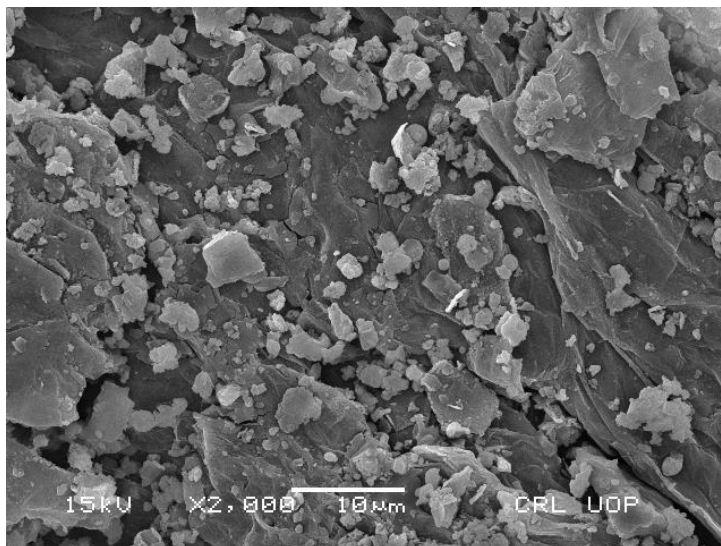
The morphologies of the synthesized materials were characterized by scanning electron microscopy (SEM). Figure 5.2 (a) represents the low magnification SEM image of

graphene oxide from this image the morphology of the secondary particles can be clearly visualized. There might be the chance of agglomeration among the particles. Fig 5.2 (b) represents the high magnification SEM image of graphene oxide. From this image, it can be seen that most of the graphite oxide has been successfully exfoliated to wavy type ultrathin structure of graphene oxide sheets.



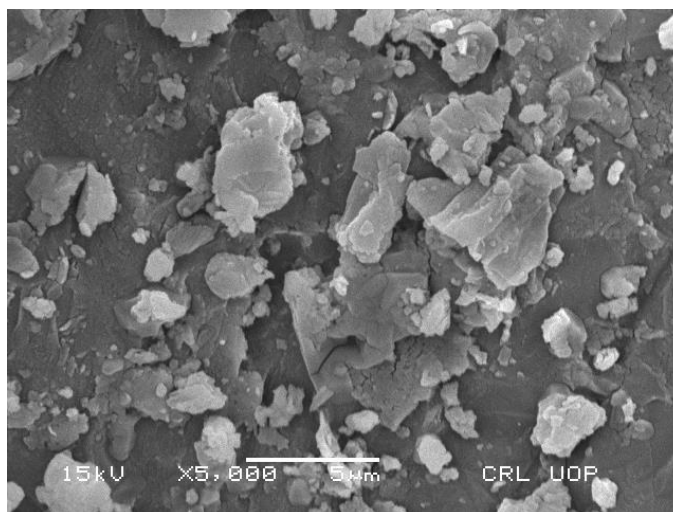
**Figure 5.2** SEM image of GO (a) low magnification (b) high magnification

Fig. 5.3 represents the SEM image of Ni/graphene nanocomposites which reveals that Ni nanoparticles are uniformly dispersed on graphene sheets.



**Figure 5.3** SEM image of Ni-G nanocomposites

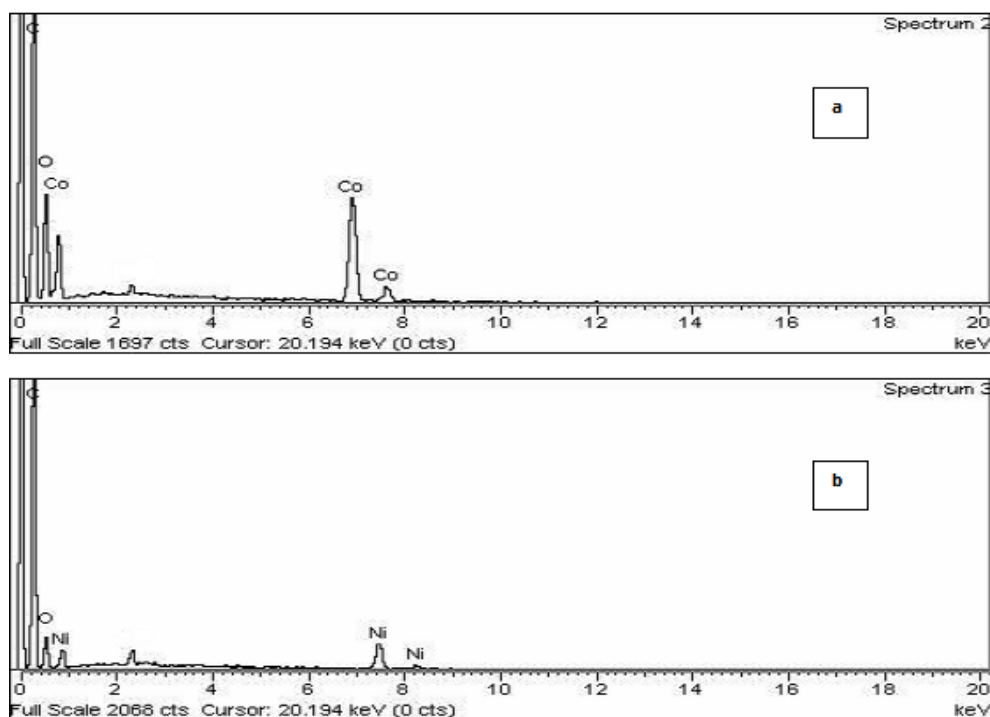
Figure. 5.4 represents the randomly dispersed Co nanoparticles on graphene sheets. It can be seen Co-G nanoparticles are randomly dispersed on ultra-thin graphene sheets. There might be chance of agglomerations among the particles.



**Figure 5.4** SEM image of Co-G nanocomposites

## 5.2 Energy-dispersive X-ray spectroscopy (EDX)

Figure 3 shows the EDX analysis of Ni/graphene and Co/graphene nanocomposites catalysts. The EDX analysis in the fig 3a shows that Co/ graphene nanocomposites catalysts was composed of C, O and Co elements. Figure 4 b represents the EDX spectrum of Ni/ graphene catalysts which reveals that Ni/graphene nanocomposites catalysts was composed of C, O and Ni elements.



**Figure 5.5** EDX analysis of (a) Co-G nanocomposites (b) Ni-G nanocomposites

The presence of carbon peaks in both the samples represents the formation of graphene sheets and small oxygen peak reveals that graphene also contains small quantity of carboxyl and hydroxyl groups.



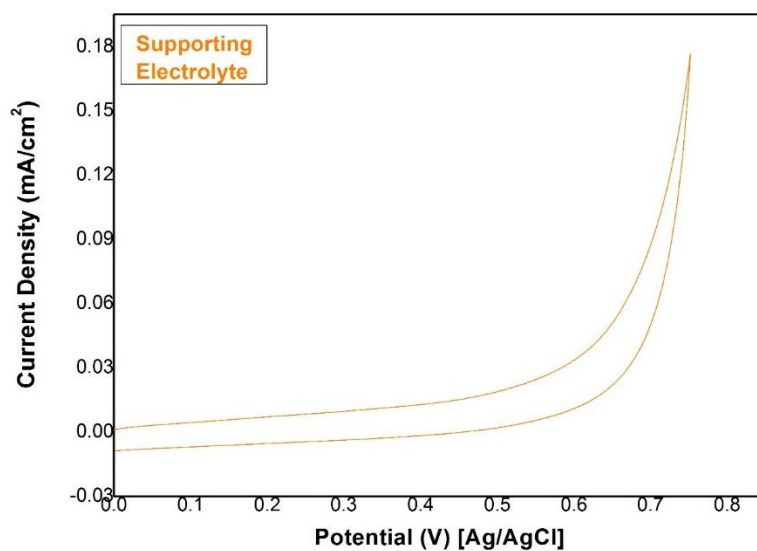
## 5.3 Cyclic Voltammetry

To investigate electrochemical behavior of prepared Ni/ graphene and Co/graphene cyclic voltammogram was recorded on two different types of electrodes later on the results were compared for the both the electrodes.

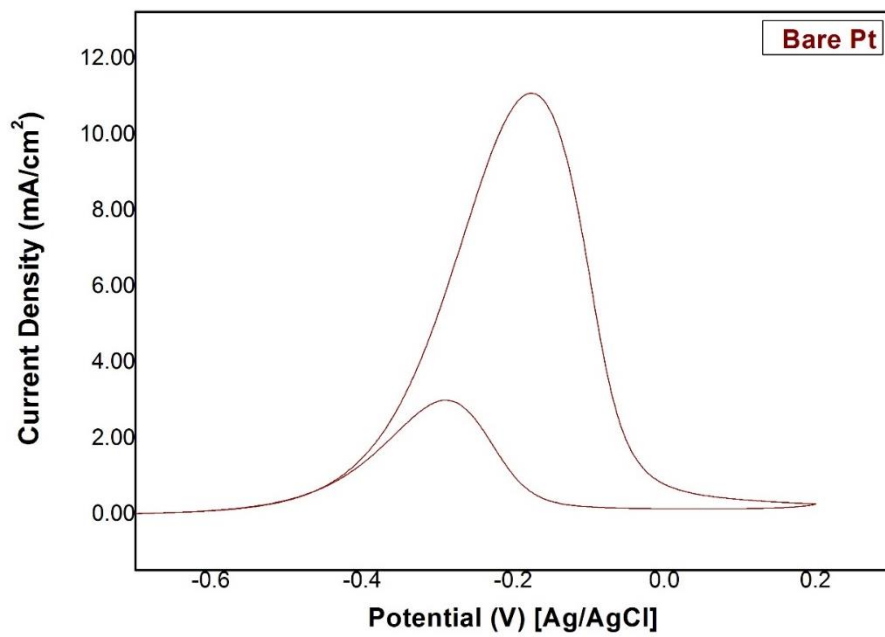
- a) Modified platinum electrode
- b) Modified Glassy Carbon electrode

### 5.3.1 CV scan on modified Platinum electrode

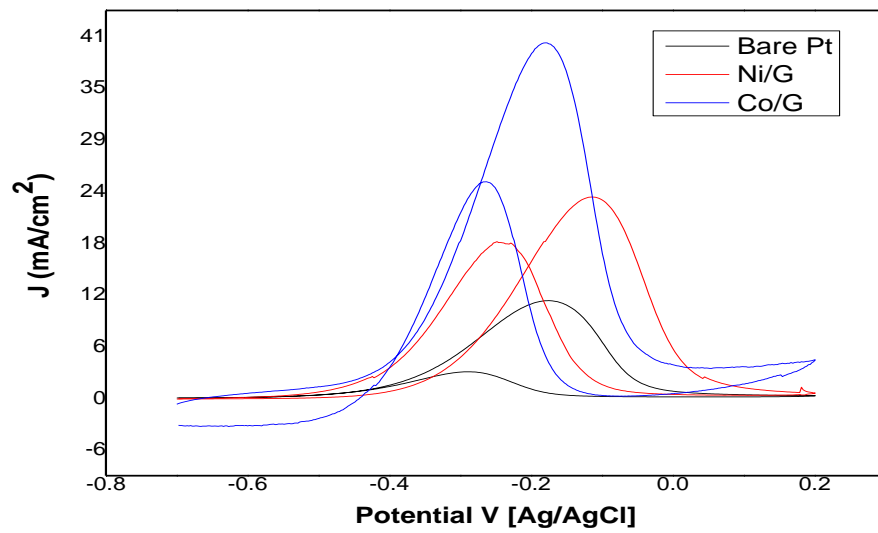
In order to investigate electrochemical behavior of prepared Ni/ graphene and Co/graphene cyclic voltammogram was recorded on modified platinum electrode as a working electrode. The cyclic voltammogram (CVs) of Ni/graphene and Co/graphene nano-composites for methanol oxidation was done in alkaline medium. For the comparison cyclic voltammogram of bare Pt electrode, Ni/ graphene and Co/graphene were recorded under same conditions at various scan rates from  $50 \text{ mVs}^{-1}$  to  $250 \text{ mVs}^{-1}$  in 1M KOH and 3M methanol concentration[3-5]..



**Figure 5.6** CV scan of supporting electrolyte



**Figure 5.7** CV scan of bare Pt electrode



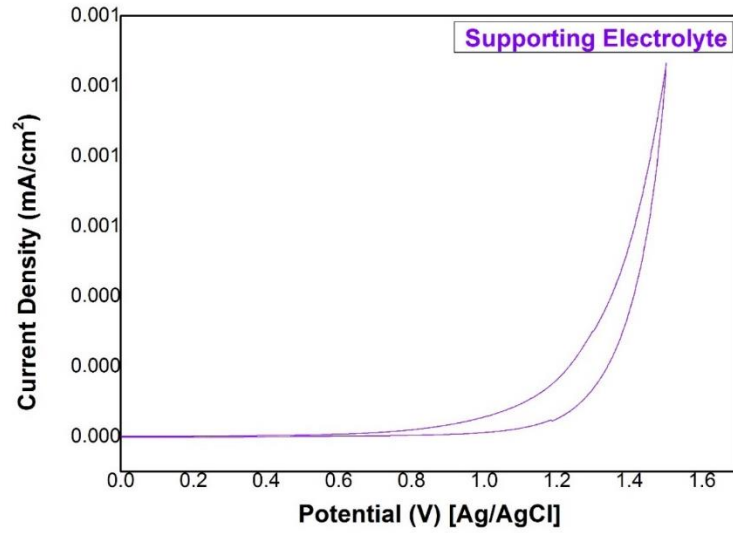
**Figure 5.8** CV scan of (a) scan of bare (b) Ni-G (c) Co-G electro-catalysts

**Table 5.1** Comparison current densities of different Electro-catalysts on Pt modified electrodes

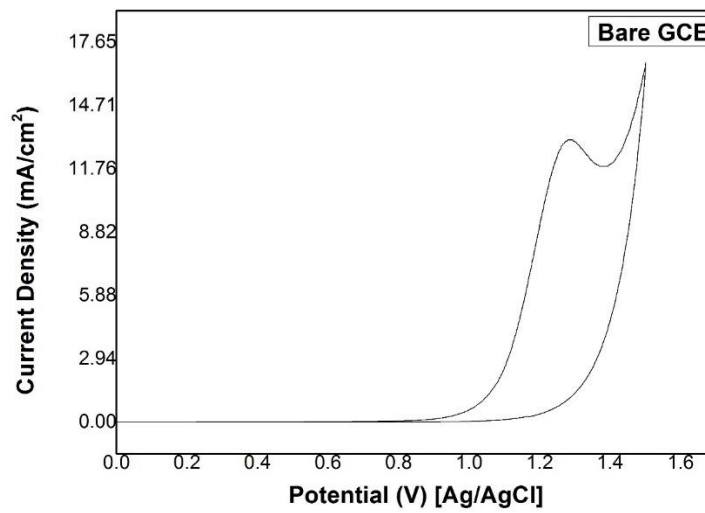
Type of Electro-catalysts used at 100mV potential	Current Density (mA/cm <sup>2</sup> )
Bare Platinum	11.5
Co/graphene on modified Pt electrode	19.5
Ni/graphene on modified Pt electrode	40

### 5.3.2 CV scan on modified Glassy Carbon electrode

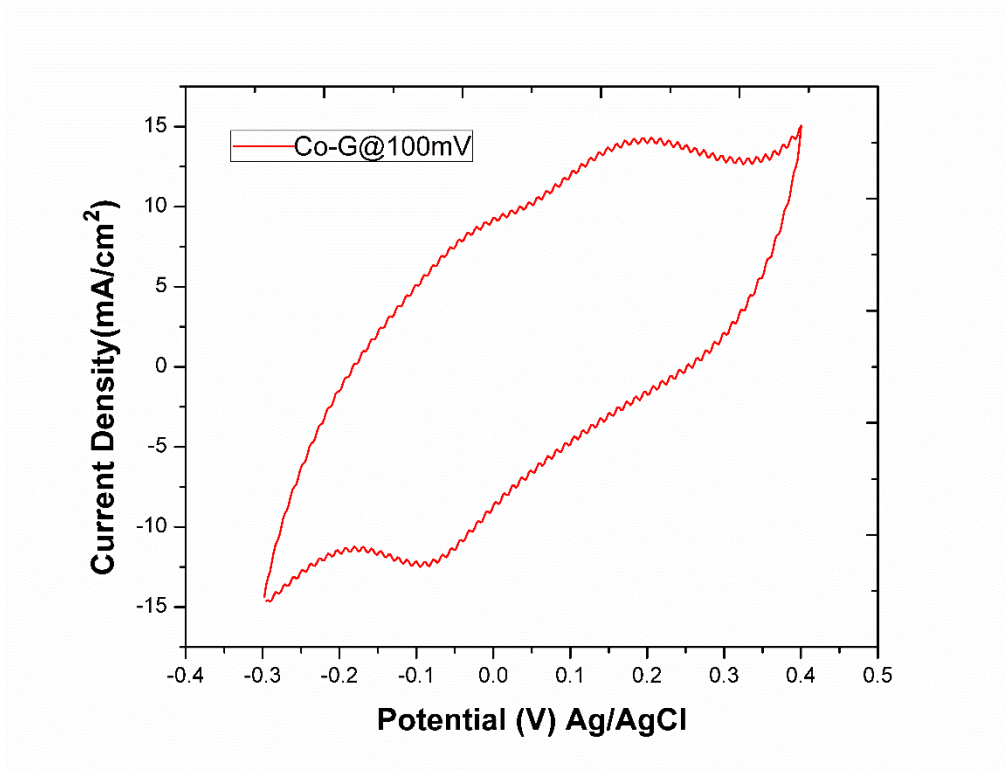
In order to investigate electrochemical behavior of prepared Co/graphene composites, cyclic voltammogram was recorded on modified glassy carbon electrode as a working electrode. The cyclic voltammogram (CVs) Co/graphene catalyst for methanol oxidation was done in alkaline medium. The cyclic voltammogram of Co/graphene was recorded under same conditions at various scan rate in 1M KOH solution containing 3M methanol concentration. Increase in current density was observed with increase in scan rate. Maximum of 25 mAcm<sup>-2</sup> current density was achieved at 250 mVs<sup>-1</sup> which shows that cobalt/graphene nanocomposites catalyst can be a better choice for methanol oxidation.



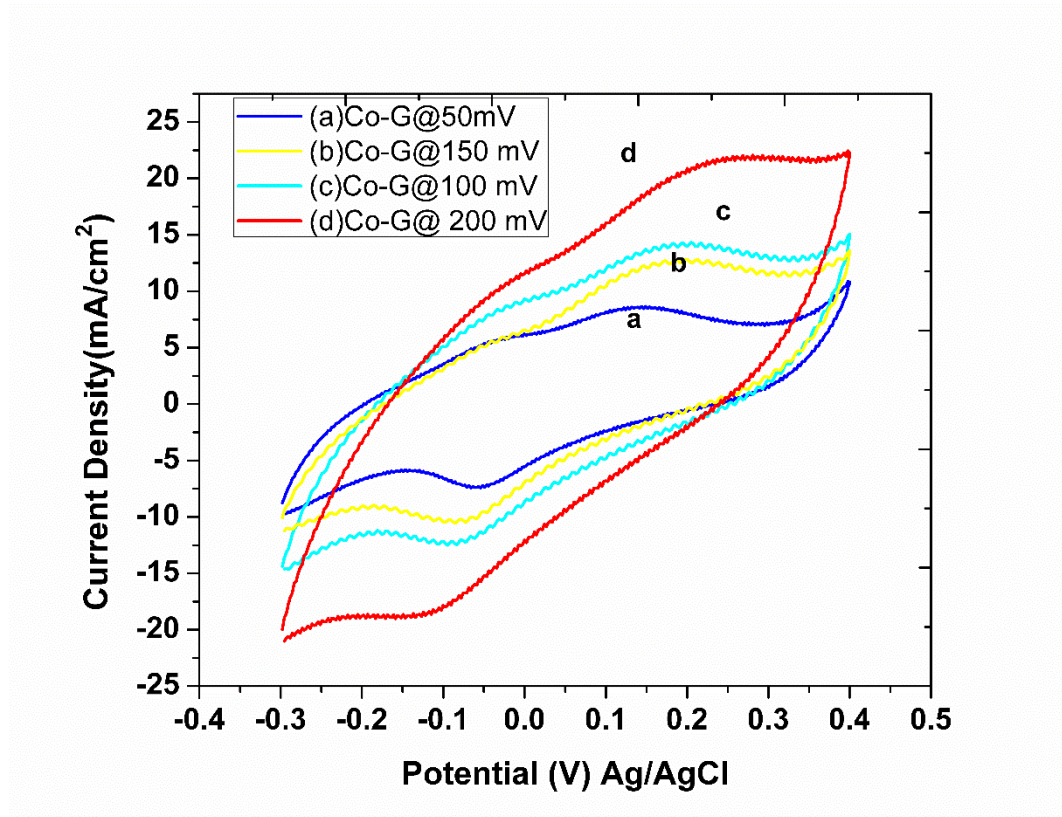
**Figure 5.9** CV scan of 1M KOH on Glassy carbon electrode



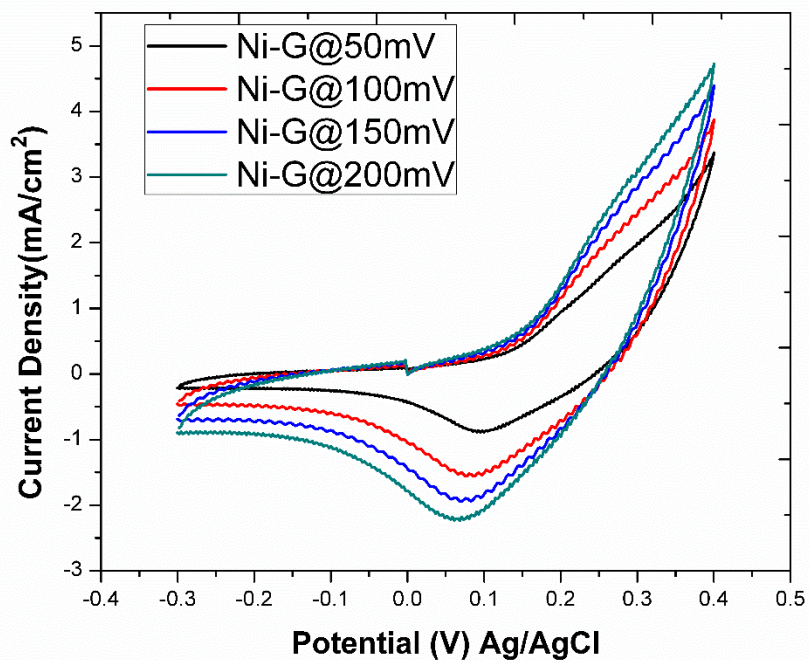
**Figure 5.10** CV scan of bare Glassy carbon electrode



**Figure 5.11** CV scan of Co-G electrocatalyst on modified Glassy carbon electrode



**Figure 5.12** CV scan of Co-G electrocatalyst on modified Glassy carbon electrode at various scan rates from 50-100 mV/s



**Figure 5.13** CV scan of Ni-G electrocatalyst on modified Glassy carbon electrode

**Table 5.2** Comparison of current densities obtained of Ni/G and Co/G electrocatalysts on GCE

Type of Electro-catalysts used	Current Density (mA/cm <sup>2</sup> )
Bare GCE	14
Co/graphene on modified glassy carbon electrode	25
Ni/graphene on modified glassy carbon electrode	15



## Summary

Ni/graphene and Co/graphene nanocomposites were synthesized by simple solution synthesis method. These synthesized nanocomposites catalysts were characterized by XRD and showed face centered cubic crystal structure. SEM micrograph of the synthesized electrocatalysts shown that nickel and cobalt nanoparticles are uniformly dispersed on graphene sheets. EDX analysis confirmed the presence of required element in the prepared samples. Later on the electrochemical properties of the synthesis electrocatalysts were investigated by cyclic voltammetry. Results were compiled on two different types of electrodes modified Pt electrode and modified glassy carbon electrode. The electrochemical oxidation of methanol were tested in alkaline medium with the help of prepared electrocatalysts. It has been observed that Co/graphene electro-catalyst showed better methanol oxidation results as compared Ni/graphene electrocatalysts. Maximum current densities were achieved at Pt modified electrode because Platinum is more efficient electron transfer rate as compared to glassy carbon electrode.

## References

- [1] Cao, Yu, et al. "One-step chemical vapor synthesis of Ni/graphene nanocomposites with excellent electromagnetic and electrocatalytic properties." *Synthetic Metals* 162.11 (2012): 968-973.
- [2] Liu, Minmin, Ruizhong Zhang, and Wei Chen. "Graphene-supported nanoelectrocatalysts for fuel cells: synthesis, properties, and applications." *Chemical reviews* 114.10 (2014): 5117-5160.
- [3] 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.
- [4] Zheng, Y. X. "Electrooxidation of propanol at the nano Ni-B amorphous alloy powder micro electrode." *J Huaqiao Univ Nat Sci* 31 (2010): 422-425.
- [5] Barakat, Nasser AM, et al. "Ni x Co 1– x alloy nanoparticle-doped carbon nanofibers as effective non-precious catalyst for ethanol oxidation." *International Journal of Hydrogen Energy* 39.1 (2014): 305-316.

## **Conclusion**

Ni/graphene and Co/graphene nanocomposites have been synthesized by using chemical reduction method from metal salts and graphene oxide, which was already prepared by the oxidation of graphite powder by using modified Hummer's method. The electrocatalytic properties of these synthesized nanocomposites for methanol oxidation were tested in alkaline medium. It has been observed that Co/graphene nanocomposites showed higher electrochemical activity as compared to Ni/graphene. However, comparing the current densities of these nanocomposites is far less than Pt/graphene which is still unbeatable as electrocatalyst for methanol oxidation reaction. Electrochemical stability and potential towards oxygen reduction reaction of these nanocomposites still need further investigations.

## **Recommendation**

The poisoning effect of the Pt catalyst significantly decreases power density and fuel consumption efficiency of the cell. To inhibit the poisoning effect and to increase the electro-oxidation rate by an order of three to four times a lot of research have been carried out to replace the Pt catalysts. Most suitable results have been achieved by alloying the Pt with Ru and Sn for the complete oxidation of methanol and CO into CO<sub>2</sub>. In recent years research is focused to develop non-noble metal electro-catalysts such as Co, Ni, Pb, and W to replace platinum an expensive metal. However above transition metals show poor oxidation kinetics. By using high conductive material as a support like graphene, carbon nanotubes (CNTs) and carbon nanofibers, electro-catalytic efficiency of these metals can be improved. Cobalt/graphene nanocomposites show better results towards methanol oxidation because of cobalt is more electropositive than platinum. Compared with other carbon support material graphene is an excellent electrode material because of its lower manufacturing cost, high surface area, and exceptional conductivity. Therefore, graphene can be used as a catalytic support material to enhance the electrochemical activity of catalyst particles for methanol and ethanol oxidation. Ni/graphene and Co/graphene nanocomposites have been synthesized by using chemical reduction method from metal salts and graphene oxide, which was already prepared by the oxidation of graphite powder by using modified Hummer's method. The electro-catalytic properties of these synthesized nanocomposites for methanol oxidation were tested in alkaline medium. It has been observed that Co/graphene nanocomposites showed higher electrochemical activity as compared to Ni/graphene. However, comparing the current densities of these nanocomposites is far less than Pt/ graphene which is still unbeatable as electro-catalyst for methanol oxidation reaction. Electrochemical stability and potential towards oxygen reduction reaction of these nanocomposites still need further investigations.

## **Acknowledgement**

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. Majid Ali and Dr. Eng. Muhammad Zubair, U.S.- 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, Quaid-i-Azam University Islamabad. 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.

# Synthesis of graphene supported cobalt nanocomposites and their applications for methanol oxidation in alkaline medium

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**Abstract**-Fuel cells are considered very attractive devices to obtain clean electrical energy directly from the chemical fuel. During the last decade much attention is given to the direct methanol fuel cells (DMFCs) because methanol is inexpensive, easily available and transported liquid fuel. Mostly platinum is employed for the electro-oxidation of methanol as an anodic material however higher economic costs and poor oxidation kinetics are the main problems of platinum based catalyst. In this paper we reported the synthesis of graphene supported cobalt nanocomposites by simple chemical solution synthesis method. The synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and EDX. The electrocatalytic properties of the synthesized catalyst for methanol oxidation were investigated in alkaline medium.

**Keywords:** Graphene, Cobalt, Direct methanol fuel cells, Nanocomposites, Electrocatalysts, Methanol oxidation.

## 1. Introduction

Under the global sustainability prospective, sustainable development involves four key factors in terms of social, environmental, economic and energy resources sustainability. Sustainable development requires sustainable supply of clean and cheap sources of energy that do not have adverse social and environmental impacts[1]. Globally, about 87% of total energy is produced by fossil fuels about 6% is generated in nuclear power plants and only 7% comes from renewable resources (hydro, wind, solar, geothermal and biofuel) [2]. Unfortunately, this planet has limited amount of fossil and nuclear energy resource and at the same time generation of energy can contribute to climate change by global warming, acid rain and ozone layer depletion[3]. In order to overcome all these critical challenges of energy

security and environmental degradation attempts have been made in the development of advance, affordable and environment friendly energy harnessing technologies. In this regard innovative energy technologies have got considerable attention during the last few decades. Among them fuel cell is considered as promising power generation technology both for mobile and stationary applications[4].

In series of fuel cells, direct methanol fuel cell (DMFC) is competitive as viable energy source in the energy market depending upon the cost, efficiency and durability of the electrocatalyst. At present, most of the fuel cells (low temperature fuel cell) use Pt-based catalyst. Due to expensive nature of Pt based electrocatalyst successful commercialization is greatly affected [5]. Beside the cost factor, Pt-based electrocatalyst also faces catalyst poisoning. Therefore researchers are trying to develop a low cost, reliable and efficient electrocatalyst to replace Pt-base catalyst[6].

So far significant numbers of studies have been performed by involving different techniques for the electro-oxidation of lower molecular weight organic compounds such as CH<sub>3</sub>OH, HCOOH, and HCHO. Results from these investigations reveals that at low temperature electro-oxidation of these organic compounds need the presence of Pt-based catalyst[7]. Two key steps dehydrogenation and chemisorption of CO are involved during the electro-oxidation of these compounds under Pt-based catalyst. A strongly adsorbed intermediate species (like CO, CHO) are produced during all these reactions. These types of species like CO, CHO are adsorbed on the surface of the catalyst and cause for catalyst poisoning[8]. The poisoning effect of the Pt catalyst significantly decreases power density and fuel consumption efficiency of the cell. To inhibit the poisoning effect and to increase the electro-oxidation rate by an order of three to four times a lot of research have been carried out to replace the Pt catalyst[9]. Most suitable results have been achieved by alloying the Pt with Ru and Sn for the complete oxidation of methanol and CO into CO<sub>2</sub> [10]. In recent years research is focused to develop non noble metal electrocatalysts such as Co, Ni, Pb, and W to replace platinum an expensive metal. However above transition metals show poor oxidation kinetics. By using high conductive material as a support like graphene, carbon nanotubes (CNTs) and carbon nanofibers, electrocatalytic efficiency of these metals can be improved. Cobalt/graphene nanocomposites show better results towards methanol oxidation because of cobalt is more electropositive than platinum[11][12][13]. Compared with other carbon support material graphene is an excellent electrode material because of its lower manufacturing cost, high surface area, and exceptional conductivity[14]. Therefore, graphene can be used as a catalytic support material to enhance the electrochemical activity of catalyst particles for methanol and ethanol oxidation[12]. Here we report the synthesis of Co/graphene nanocomposites by a facile, economic and environmental friendly method. Furthermore, the synthesized material was characterized by XRD, SEM and EDX. The electrochemical activity of the synthesized electrocatalyst towards methanol oxidation was characterized in alkaline medium.

## **2. Experimental**

### *2.1 Material and Reagents*

Graphite Powder (99.99%) of particle size 45  $\mu\text{m}$ , H<sub>2</sub>SO<sub>4</sub> (98%), NaNO<sub>3</sub> (99%), KMnO<sub>4</sub> (99%), H<sub>2</sub>O<sub>2</sub> (30%), Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Ethylene Glycol, NH<sub>3</sub>(25%) solution were purchased

from Sigma Aldrich. All the reagents were of analytical grades and used without further purification.

## 2.2 Preparation of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder by modified Hummer's method [15]. In the typical procedure 1g of graphite powder (99.99%) was mixed with 25ml 98 % sulphuric acid ( $H_2SO_4$ ), and 1g of sodium nitrate ( $NaNO_3$ ) in an ice bath for 3h. Then 5g of  $KMnO_4$  was added gradually in above mixture. The reaction was kept under vigorous stirring at 30 °C. 100ml of water was added slowly and the product was placed at 85°C for 2h. Then reaction was treated with 10ml of hydrogen peroxide ( $H_2O_2$  30 %). Finally, the obtained yellowish mixture was centrifuged and washed several times with distilled water and ethanol in order to get pure grapheme oxide (GO).

## 2.3 Preparation of Co/ Graphene nanocomposites

Co/ Graphene nanocomposites catalyst was synthesized by using simple solution synthesis method[13]. In this procedure, 290mg of cobalt nitrate hexa-hydrate ( $Co(NO_3)_2 \cdot 6H_2O$ ), and 100mg of graphene oxide were added in a 100ml flask having 60ml ethylene glycol as a solvent.

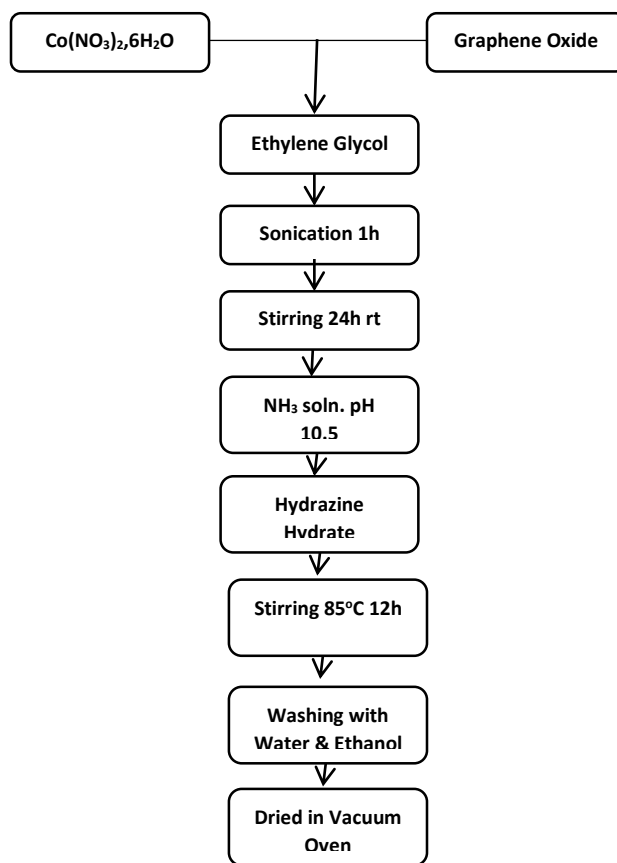


Figure 1 Schematic flow diagram Co/graphene nanocomposites synthesis



After ultra-sonication for an hour, the mixture was stirred for 24 hours at ambient temperature. The small amount of ammonia solution (25%) was added gradually to adjust pH of the solution to 10.5. After that 1.0 ml hydrazine hydrate was added as a reducing agent into the mixture and the reduction reaction was performed under constant stirring at 85°C for 12 h. The obtained product was then filtered, washed several times with distilled water and ethanol. The product was dried in a vacuum desiccator at room temperature.

#### 2.4 SEM /XRD Characterization

In order to investigate the phase, crystal structure and lattice parameter of the prepared nanocomposites, X-ray powder diffractometer (STOE Germany) with computer interface was used having radiation source Cu K $\alpha$  at  $\lambda = 1.5418 \text{ \AA}$ . The scan angle  $2\theta$  was selected  $0^\circ$ - $80^\circ$  with step size 0.04/sec.

To study the surface morphology of the synthesized catalyst Scanning Electron Microscope (HITACHI SU- 1500) and voltage was kept up-to 15 kV.

#### 2.5 Electrochemical Measurements

All the electrochemical measurements were performed by using AUTOLAB 4.9 Potentiostat connected to PC. Ag/AgCl electrode was used as reference electrode in this work. The counter electrode was a Pt wire 1mm thick and 12cm long. 1M KOH solution was used as a supporting electrolyte with 3M methanol concentration in a conventional three-electrode Pyrex glass electrochemical cell. The electrochemical characterization of the prepared Co/graphene nanocomposites was done by using cyclic voltammetry technique. The obtained current densities were normalized based on the utilized surface area of the modified glassy carbon electrode. The response of peak current was checked at various scan rates ranging from  $50\text{mVs}^{-1}$  to  $250\text{mVs}^{-1}$  at starting potential starting from 0 mV to 1800 mV positive vertex potential.

#### 2.6 Preparation of working electrode (GCE)

In the present work, glassy carbon electrode with active area  $0.071 \text{ cm}^2$  was modified as working electrode. The working electrode was first washed and cleaned with distilled water than polished with alumina slurry. For the modification of working electrode homogenous slurry of the functional material was prepared by mixing 2 mg fine powder of the active material, 20 $\mu\text{l}$  of nafion solution and 400 $\mu\text{l}$  of isopropanol. After sonicating the slurry for 30 minute at room temperature, 15 $\mu\text{l}$  from the prepared slurry was poured on the active surface of the glassy carbon electrode which was then air dried at room temperature.

### Result and Discussion

Co/grapheme nanocomposites catalyst was characterized by performing X- ray diffraction and scanning electron microscopy. XRD pattern of graphene oxide (GO) is shown in the figure 1(a). The characteristic peak is obtained at  $2\theta$  of  $11.5^\circ$  clearly indicates the synthesis of graphene oxide, which shows that effective oxidation of graphite leads to the formation of graphene oxide. The XRD pattern of prepared Co/graphene nanocomposites is shown in the Fig.1. (b) The typical reflection peak at  $2\theta = 22.3^\circ$  indicates the formation of

graphene by the reduction process of graphene oxide. On the other hand, the diffraction bands obtained at  $2\theta = 37.4^\circ$ ,  $44.3^\circ$  and  $63.2^\circ$ ,  $76.1^\circ$  can be assigned to the characteristic of face center cubic (fcc) structure of Co nanoparticles[16].

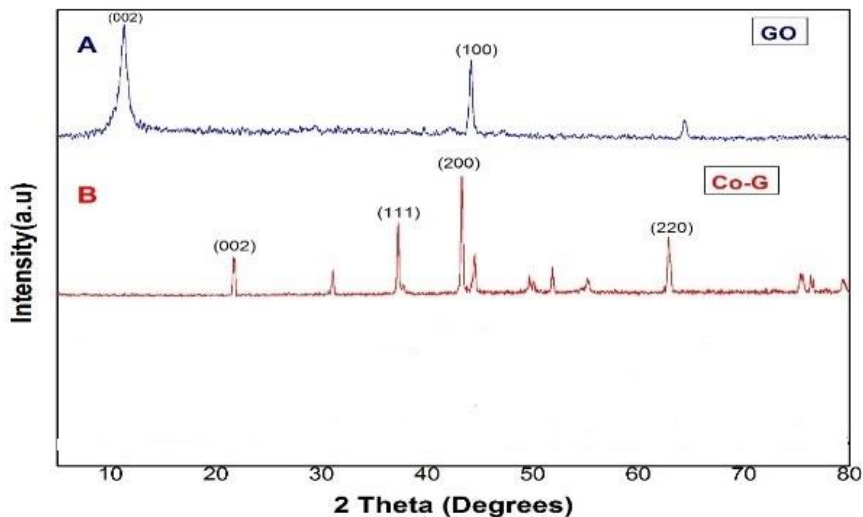


Fig. 2 XRD pattern (A) graphene oxide (B) Co/graphene nanocomposites

The morphologies of the synthesized materials were characterized by scanning electron microscopy (SEM). Figure.2 (a) represents t SEM image of graphene oxide. From this image it can be seen that most of the graphite oxide has been successfully exfoliated to wavy type ultrathin structure of graphene oxide sheets. Figure. 2 (b) represents the randomly dispersed Co nanoparticles on graphene sheets

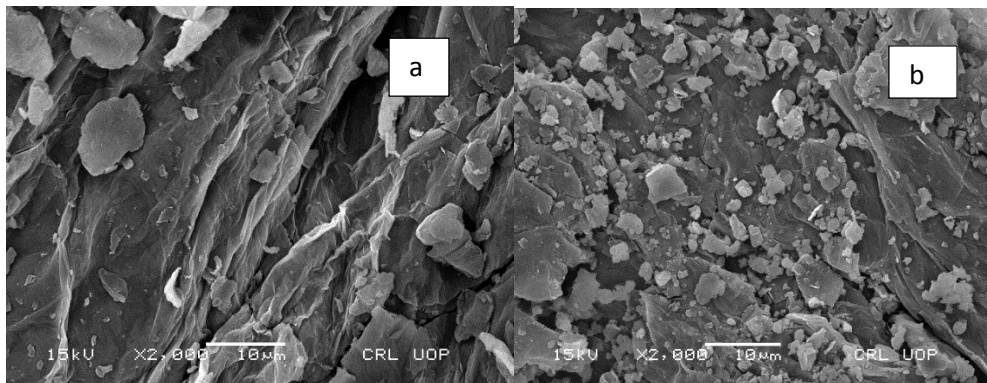


Fig. 3 (a) SEM image of graphene oxide (b) SEM image of Co/graphene nanocomposites

Figure 3 shows the EDX analysis of Co/graphene nanocomposites. The EDX analysis in the fig 3 shows that Co/ graphene nanocomposites catalyst was composed of C, O and Co elements.

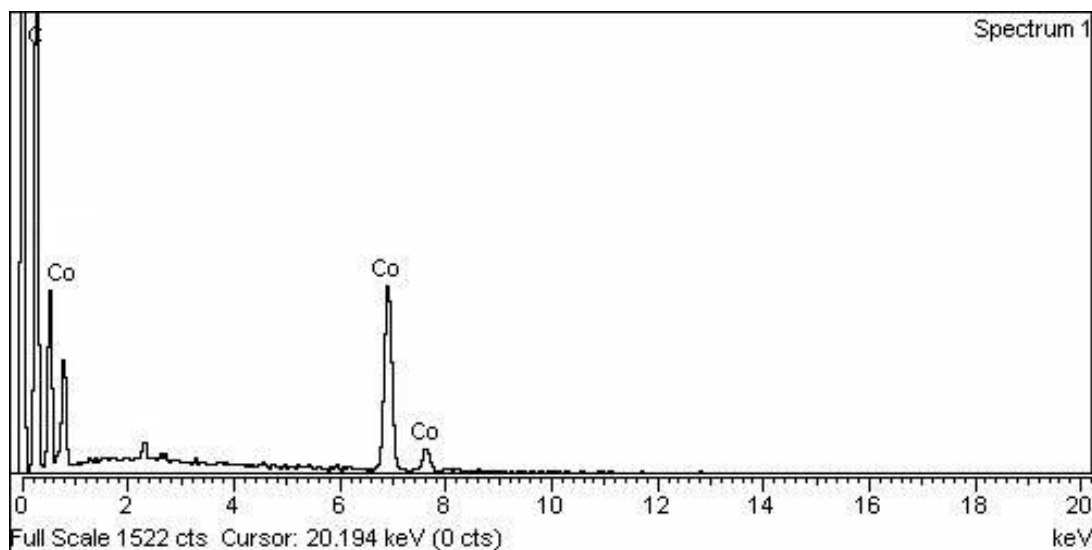


Fig. 4 EDX analysis of Co/graphene nanocomposites

. The presence of carbon peaks in sample represents the formation of graphene sheets and small oxygen peak reveals that graphene also contains small quantity of carboxyl and hydroxyl groups.

### 2.7 Cyclic Voltammetry

In order to investigate electrochemical behavior of prepared Co/graphene composites, cyclic voltammogram was recorded on modified glassy carbon electrode as a working electrode. The cyclic voltammogram (CVs) Co/graphene catalyst for methanol oxidation was done in alkaline medium. The cyclic voltammogram of Co/graphene was recorded under same conditions at various scan rate in 1M KOH solution containing 3M methanol concentration. A current density of  $25\text{mAcm}^{-2}$  was recorded at  $250\text{mVs}^{-1}$  which shows that cobalt/graphene nanocomposites catalyst can be a better choice to replace platinum and alloy catalysts.

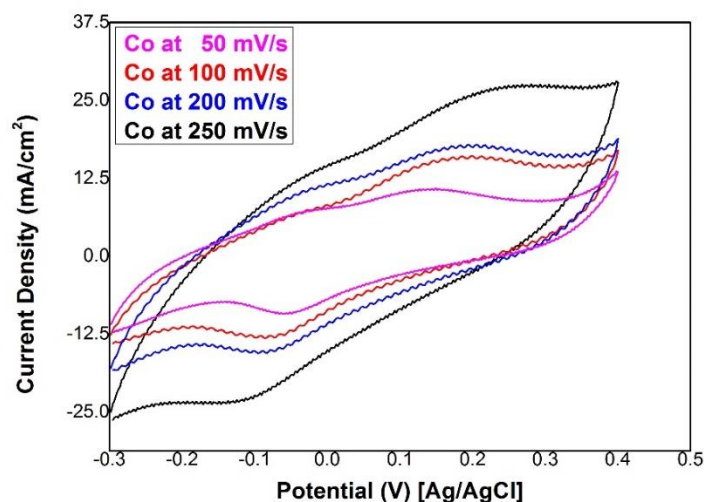


Figure 5 CVs of Co/graphene catalyst in 1M KOH solution containing 3M methanol at various scan rates

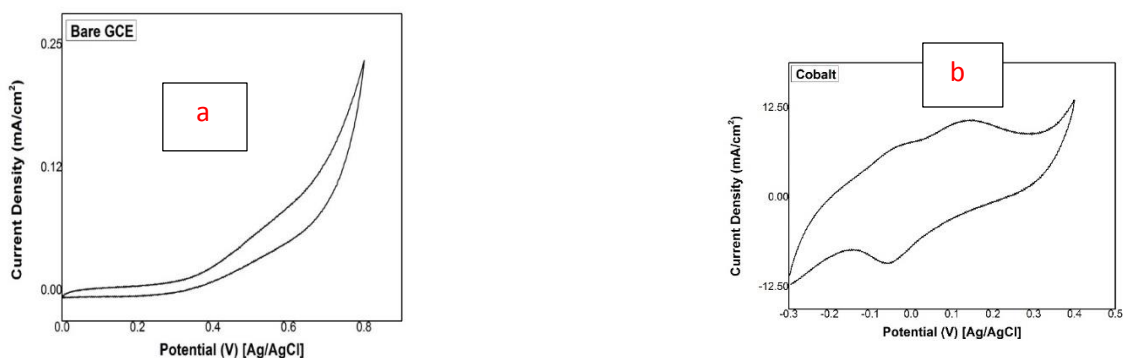


Figure 6 (a) CVs of bare GCE b) Co/graphene catalyst in 1M KOH solution containing 3M methanol at 50 mVs<sup>-1</sup>

Cyclic voltammogram of bare GCE is shown in the figure 6 (a) which indicates a very low peak current density of 0.25 mAcm<sup>-2</sup> at 50 mVs<sup>-1</sup>. After modification of GCE with active material 2mg of Co/graphene catalyst a peak current density of 12.50 mAcm<sup>-2</sup> was achieved at 50 mVs<sup>-1</sup> as shown in the figure 6 (b). The dramatic increase in the peak the current density shows the excellent oxidation potential of Co/graphene catalyst toward methanol oxidation. The anodic peak current observed for the period of forward scan was due to the electro-oxidation of methanol into intermediate species and further complete oxidation of these species into CO<sub>2</sub>, H<sub>2</sub>O and electrons. During the reverse scan, oxidation peak is obtained due to the remaining species that was not fully oxidized during the forward scan.

### 3. Conclusion

Co/graphene nanocomposites catalyst was synthesized by using chemical reduction method from metal salts and graphene oxide. The electrocatalytic properties of this synthesized catalyst for methanol oxidation was tested in alkaline medium. It has been observed that Co/graphene nanocomposites showed excellent electrocatalytic activity towards methanol oxidation. Electrochemical stability and potential towards oxygen reduction reaction of these nanocomposites catalysts still need further investigations.

## Acknowledgements

This work was financially supported by PGP and Research Directorates of NUST. We also acknowledge the School of Chemical & Materials Engineering (SCME) NUST for their research facilities.

## References

- [1] I. Dincer, "Environmental and sustainability aspects of hydrogen and fuel cell systems," no. August 2006, pp. 29–55, 2007.
- [2] I. Transactions, E. Conversion, and S. Univer, "Environmental Impacts of Electricity Generation : A Global Perspective Environmental Impacts of Electricity Generation ;," no. September, 2016.
- [3] B. K. Bose, "Energy, Environmental Pollution, and the Impact of Power Electronics," no. March, pp. 6–17, 2010.
- [4] O. Z. Sharaf and M. F. Orhan, "An overview of fuel cell technology : Fundamentals and applications," *Renew. Sustain. Energy Rev.*, vol. 32, pp. 810–853, 2014.
- [5] H. Liu, C. Song, L. Zhang, and J. Zhang, "A review of anode catalysis in the direct methanol fuel cell," no. April, 2006.
- [6] N. A. M. Barakat, M. Motlak, B. Kim, A. G. El-deen, S. S. Al-deyab, and A. M. Hamza, "Journal of Molecular Catalysis A : Chemical Carbon nanofibers doped by Ni x Co 1 – x alloy nanoparticles as effective and stable non precious electrocatalyst for methanol oxidation in alkaline media," *Journal Mol. Catal. A, Chem.*, vol. 394, pp. 177–187, 2014.
- [7] N. A. M. Barakat, M. Motlak, A. A. Elzatahry, K. Abdelrazek, and E. A. M. Abdelghani, "ScienceDirect Ni x Co 1 L x alloy nanoparticle-doped carbon nanofibers as effective non-precious catalyst for ethanol oxidation," *Int. J. Hydrogen Energy*, vol. 39, no. 1, pp. 305–316, 2013.
- [8] A. S. Aricò, S. Srinivasan, and V. Antonucci, "DMFCs : From Fundamental Aspects to Technology Development," no. 2, pp. 133–161, 2001.
- [9] P. O. Box and C. Ch, "Shell Research Limited, Thornton Research Centre, P.O. Box 1, Chester CH1 3SH, England," vol. 118, 1981.
- [10] E. V. Spinacé, M. Linardi, and A. O. Neto, "Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt-Sn electrocatalysts," *Electrochem. commun.*, vol. 7, no. 4, pp. 365–369, 2005.
- [11] A. A. Elzatahry, A. M. Abdullah, T. A. S. El-din, and A. M. Al-enizi, "Nanocomposite Graphene-Based Material for Fuel Cell Applications," vol. 7, pp. 3115–3126, 2012.
- [12] Z. Wang, Y. Du, F. Zhang, Z. Zheng, Y. Zhang, and C. Wang, "High electrocatalytic activity of non-noble

- Ni-Co/graphene catalyst for direct ethanol fuel cells.," *Sect. Title Electrochem. Radiational, Therm. Energy Technol.*, vol. 17, no. 1, pp. 99–107, 2013.
- [13] N. A. M. Barakat and M. Motlak, "Applied Catalysis B : Environmental Co x Ni y -decorated graphene as novel , stable and super effective non-precious electro-catalyst for methanol oxidation," *Applied Catal. B, Environ.*, vol. 154–155, pp. 221–231, 2014.
- [14] W. Gao, "The chemistry of graphene oxide," *Graphene Oxide Reduct. Recipes, Spectrosc. Appl.*, pp. 61–95, 2015.
- [15] D. C. Marcano, D. V Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, "Improved Synthesis of Graphene Oxide," vol. 4, no. 8.
- [16] J. Wu, D. Zhang, Y. Wang, Y. Wan, and B. Hou, "Catalytic activity of graphene-cobalt hydroxide composite for oxygen reduction reaction in alkaline media," *J. Power Sources*, vol. 198, pp. 122–126, 2012.