CHAPTER 1

INTRODUCTION

The energy demand in today's world is increasing rapidly due to the increased human population and thereby causing global warming and environmental degradation. At present, the majority of the world energy demand is fulfilled by fossil fuels like coal, natural gas and crude oil. According to the International Energy Outlook 2019 (IEO, 2019), world energy demand is projected to rise by almost 50 % from 2019 to 2050. The major amount of energy is consumed by non-organization of Economic Cooperation and Development (OECD) countries, where consumption is driven by strong economic growth, increased access to marketed energy, and rapid population growth. The maximum energy consumption in non-OECD countries like India, South Asia, Africa and China will increase by 70 % from 2018 to 2050 in comparison to only 15 % increase in OECD countries like Australia and New Zealand, United States, South Korea and Canada (IEO, 2019). However, the renewable energy sources are the fastest-growing form of energy in the world. The reported global consumption of renewable energy resources is rising by 3 % per year from 2018 and will continue till 2050 (IEO, 2019). It is expected that as a share of primary energy consumption in the world, the renewable energy sources will significantly increase by 2050.

Currently, the world energy demand is met by fossil fuels such as coal (26.9 %), petroleum (31.6 %) and natural gas (22.8 %) (Key World Energy Statistics, 2020). Whereas, nuclear energy supplies around 4.9 % and renewable energy resources such as biofuels, hydropower, solar, wind, geothermal combined all supply around 13.8 % of the total energy demand (Key World Energy Statistics, 2020). It is clear from the reported

published literature that the fossil fuels are still considered as the primary sources of energy due to their several short term benefits like abundance in nature in large quantities, cheap energy sources, useful by-products and they store and deliver large amounts of energy more efficiently and consistently than current alternative energy sources (Wang and Economides, 2013). However, the widespread use of fossil fuels negatively affects nature due to the release of gaseous pollutants like CO_2, SO_X and NO_X into the atmosphere (Munawer, 2018). Moreover, the reserves of fossil fuels are limited and it will be depleted soon if not switched over to alternative sources of energy. Thus, to motivate the sustainable development of economy along with the preservation of the healthy environment for our next generation, there is a great need to focus on renewable energy sources (Zhu et al., 2019 and Das et al., 2020).

Unfortunately, the use of energy from the renewable resources are based on current technological developments which encounters several obstacles such as availability of sources, high costs, and intermittency (Kwok et al., 2019). However, at the present time due to growing concern on global environmental issues has led scientists to leverage energy from new, renewable, efficient, easily accessible and more environmentally friendly energy sources through alternative means (Caglar and Kivrak, 2019 and Romero-Cano et al., 2019). In this context, fuel cell device is considered as a promising candidate to produce stable electricity in a clean, efficient, and sustainable manner without any contamination of the environment. Thus, it has attracted the attention of researchers around the world for research and development work on fuel cell to produce low-cost electrical energy through the development of efficient and cheaper cell components like electrocatalyst materials, membrane electrolyte and bipolar plates, etc (Olu et al., 2016, Siahroudi et al., 2020, Gupta and Pramanik, 2019 and Wang et al., 2019).

The fuel cells are electrochemical devices that convert the chemical energy contained in the externally supplied fuel and oxidant directly into electrical energy and heat through electrooxidation of fuel at anode and reduction reactions at the cathode in the presence of oxidant (Vyas et al., 2019). The typical schematic representation of direct ethanol fuel cell is shown in Fig (1.1). The anode and cathode of the fuel cell consist of active electrocatalyst materials, mainly platinum (Pt) based.
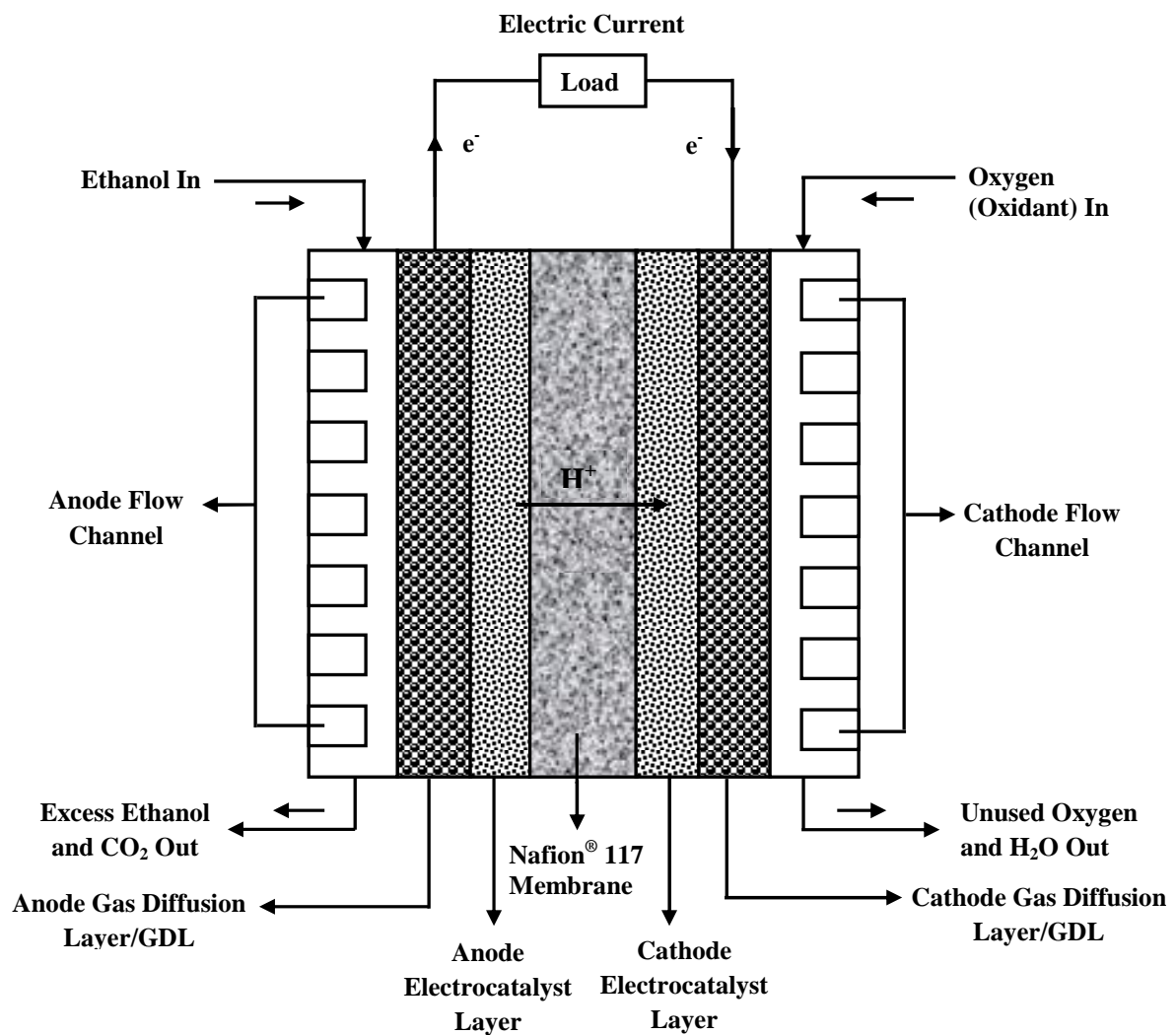

Figure 1.1 Schematic of a direct ethanol fuel cell.

The active components i.e., electrocatalyst materials are coated on an electrically conducting porous substrate or gas diffusion layer (GDL) with carbon microporous layer (MPL) to manufacture anode and cathode electrodes using suitable electrocatalyst depending upon the fuel cell or oxidant to be used in fuel cells. The ion-permeable membrane electrolyte medium is sandwiched between an anode and cathode which is known as membrane electrode assembly (MEA) (Fig 1.1). The fuels are mainly hydrogen or hydrogen rich molecules i.e., methanol and ethanol are fed to the anode side, and the oxidant is delivered to the cathode side (Pramanik and Basu, 2007, Pramanik et al., 2008 and Gupta and Pramanik, 2019).

The electrolyte may be acidic or alkaline in nature. However, acidic electrolyte Nafion$^{®}$ is very popular and widely used solid electrolyte material which is highly conducting (0.1 Scm^{-1}) and transport ions through it. The electrooxidation of fuel at the anode produces hydrogen ions/protons (H^{+}) and electrons (e^{-}) when the acidic medium is used as an electrolyte such as Nafion$^{®}$. The electrons pass through the external circuit in the direction of the cathode and create an electrical current. The hydrogen ions (H^{+}) pass through the conductive membrane electrolyte from the anode side to the cathode side. The hydrogen ions (H^{+}) and electrons (e^{-}) combine at cathode with oxidants such as oxygen supplied from an external source resulting in formation of water and heat.

In fuel cell operation, the fuel is electrochemically split at the electrode surface with high electrical power and resulting in lower energy losses compared to direct combustion of fuels in internal combustion (IC) engines. The architecture of the single-step conversion of chemical energy of supplied fuels to electrical energy in fuel cells compared to the multi-step involved in conventional combustion heat engines offers many unique advantages (Sharaf and Orhan, 2014). In short, fuel cells offer a cleaner, more efficient

and possibly more flexible conversion of chemical form of energy to electrical energy. Thus, it has a high potential for replacing existing fossil fuel-based combustion engines operating on for powering vehicles, potable appliances and stationary power sources. Although, fuel cells are the oldest technologies for converting energy, the exact origin is obscure. The first working prototype of a fuel cell was developed by Sir William Robert Grove, a lawyer and an amateur scientist (Larmine and Dicks, 2003). The first known demonstration of the principals of a hydrogen fuel cell was conducted separately by W.R Grove and Christian Friedrich Schonbein in 1839 (Sharaf and Orhan, 2014). Since then the researchers and scientific community are endlessly working to design and develop a wide variety of fuel cells those could provide a feasible solution for practical applications along with low cost, high efficiency and reliability (Larmine and Dicks, 2003 and Pramanik et al., 2008).

The fuel cells are mainly classified according to (i) the electrolyte material used in the cell like proton exchange membrane fuel cell (PEMFC), alkaline fuel cells (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC), (ii) the fuels used at the anode electrode i.e., direct ethanol fuel cell (DEFC) and direct methanol fuel cell (DMFC) based on the ethanol and methanol fuel used at the anode, respectively and (iii) the operating temperature range i.e., high-temperature fuel cells (600-1000 °C) includes SOFC and MCFC and low temperature fuel cells (room temperature of 25 °C to 220 °C) includes remaining fuel cells such as PEMFC, AFC and PAFC (Sharaf and Orhan, 2014). The high-temperature fuel cells e.g., SOFC and MCFC are difficult to fabricate and run due to mechanical and chemical compatibility problems of cells along with long start-up and cooling times. On the other hand, low-temperature fuel cells are easy to fabricate and run. As a consequence, they have no issue with

material selection (Mekhilef et al., 2012). In this perspective, the most promising energy conversion devices to date are low temperature fuel cells based on polymer electrolyte membrane and operated with anode fuels mainly hydrogen or hydrogen-rich molecules such as methanol, ethanol, acetic acid, and $NaBH_4$, etc (Lamy et al., 2001, Pramanik and Basu, 2007 and Olu et al., 2016). Among all the low-temperature fuel cells, direct alcohol fuel cell (DAFC) have gained significant attention due to many positive aspects such as low emissions of contaminants, high energy density, and ease of handling and storage of liquid fuel (Lamy et al., 2004, Kamarudin et al., 2013 and Gupta and Pramanik., 2019). Some low molecular-weight aliphatic alcohols, such as methanol and ethanol, have been used as fuel in direct alcohol fuel cell (DAFC) based on the proton exchange membrane (PEM) (Lamy et al., 2002, Pramanik and Basu, 2007 and Kamarudin et al., 2013). The most commonly used electrolyte material is Nafion® based membranes manufactured by DuPont® (USA). The acidic medium is selected in DEFC due to higher ionic conductivity, quick start-up, less sensitive to contaminants and high power density (Ong et al., 2017).

As already mentioned, among the various aliphatic alcohols methanol and ethanol are widely used in PEMFC instead of hydrogen, which is the ultimate fuel for the future sustainable energy supply. Methanol being an organic liquid fuel has many benefits over hydrogen, such as high aqueous electrolyte solubility, low cost, ease of handling, transport and storage. The energy density of methanol is about 6.1 kWh kg^{-1}. However, methanol is neurotoxic, volatile, flammable, non-renewable, and environmentally hazardous and offers a crossover to the cathode through the polymeric membrane electrolyte resulting in an overall reduction in fuel cell output. It is also synthesized from non-renewable sources (synthesis gas, CO + H_2) through a chemical path (Pramanik and

Basu, 2007, Pramanik et al., 2008 and Gupta and Pramanik, 2019). On the other hand, ethanol is an especially promising viable liquid fuel that can be widely used in PEMFC, as ethanol provides many advantages over methanol fuel such as non-toxic, safer, higher potential energy density (8.01 kWh kg^{-1} vs. 6.1 kWh kg^{-1}), lower volatility and a little higher boiling point than methanol. In addition, the permeation of ethanol through the polymeric membrane is lower compared to methanol due to a larger molecular size and therefore the cathode performance is less severely affected than that of methanol. Moreover, ethanol is renewable and can be generated abundantly from sustainable biomass sources such as sugar cane, maize, wheat, and beet through fermentation (Pramanik and Basu, 2007, Gupta and Pramanik, 2019 and Almeida et al., 2019). Thus, the ethanol was selected as a fuel for the direct ethanol fuel cell in the present research work. The theoretical open circuit voltage (OCV) of the DEFC at standard temperature and pressure (STP) conditions is 1.145 V, which is very close to the OCV of direct methanol fuel cell (1.213 V) (Lamy et al., 2001). It is clear from the following electrooxidation reaction (Equation 1.1) that one molecule of ethanol releases 12 electrons and thus, electrical current produced per molecule of ethanol is higher than the methanol molecule.

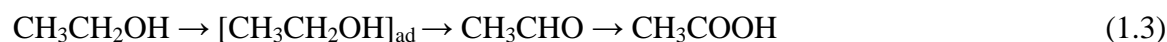$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \tag{1.1}$$

However, the electrooxidation of ethanol fuel presents many challenges, such as the difficulty of splitting C–C bond of ethanol molecule and the slow ethanol electrooxidation kinetics at low temperature on the present Pt-based electrocatalyst (Kutz et al., 2011 and Rizo et al., 2017a). The DEFC performance in terms of power density and current density get reduced due to slow ethanol electrooxidation kinetics. Thus, development of suitable electrocatalyst is required to achieve very high power density from the developed DEFC

at low and moderate temperature. As stated in the literature, ethanol electrooxidation reactions in the acid medium undergo parallel and successive oxidation reactions due to the presence of a C–C bond in the ethanol molecule. The breaking of C–C bond in the ethanol molecule through the electrochemical reaction process is kinetically obstructed due to many reasons, such as geometric inaccessibility, low electron affinity, and ionization energy between two atoms (Mann et al., 2006 and Shen et al., 2010). Generally, aqueous solution of ethanol is fed to the anode electrode of a DEFC where electrooxidation of ethanol molecule through a specific electrochemical pathways release electrons (e^-) and protons (H^+). The reaction pathways may be due to complete electrooxidation (Equation 1.2) or partial electrooxidation (Equation 1.3).

Total oxidation:

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow C_{1ads}, C_{2ads} \rightarrow CO_2 \qquad (1.2)$$

Partial oxidation:

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow CH_3CHO \rightarrow CH_3COOH \qquad (1.3)$$

where C_{1ads} and C_{2ads} are the adsorbed intermediate species on the electrocatalyst sites with one or two carbon atoms. As a result of partial oxidation, which occurs through parallel and incomplete pathways (Equation 1.3) generates four electrons ($4e^-$) followed by the formation of intermediates such as acetaldehyde and acetic acid instead of the final product carbon dioxide which would form due to complete electrooxidation (Equations 1.1 and 1.2) (Lamy et al., 2001, Pramanik and Basu, 2007, Kutz et al., 2011 and Vyas et al., 2019). The intermediates species i.e., C_{1ads} and C_{2ads} formed (Equation 1.2) by the scission of the C-C bond results in the formation of CO_2 in the presence of an active electrocatalyst. However, inefficient and less active electrocatalyst tends to strongly adsorb mono carbon intermediate species such as CO_{ads} and $CH_{x,ads}$ on the Pt surface

which prevent the further adsorption of additional ethanol molecules (Torrero et al., 2016 and Farsadrooh et al., 2018). Complete electrooxidation of ethanol is therefore hindered and partially oxidized molecules such as acetic acid (CH_3COOH) and acetaldehyde (CH_3CHO) are the most abundant products generated during ethanol electrooxidation (Equation 1.3) (Kutz et al., 2011 and Wnuk and Lewera, 2019). Only part of the chemical energy contained in ethanol fuel is converted into electrical energy via partial electrooxidation route (Equation 1.3). Under typical fuel cell conditions, CO_{ads} and acetaldehyde (CH_3CHO) can be further oxidized to CO_2, whereas acetic acid (CH_3COOH) can not be oxidized to CO_2 as acetic acid appears to be a dead-end ethanol electrooxidation product in an acidic medium (Kutz et al., 2011, Torrero et al., 2016, Wnuk and Lewera, 2019 and Zhu et al., 2019). Synthesis of suitable electrocatalysts with appropriate metal selection and their various combinations could effectively breakdown the C-C bond of ethanol and favors the formation of final product CO_2 from the adsorbed intermediate CO_{ads}.

To date, rare and precious platinum has been primarily used for ethanol electrooxidation in the acidic medium as active electrocatalyst material due to its ability to break organic molecules after favorable chemisorptions. However, it suffers from significant activation over-potential, slow electrooxidation rate kinetics, and the formation of partially oxidized intermediates (CO and CH_x) that is strongly adsorbed on the electrocatalyst surface blocking active sites (Vigier et al., 2004 and Almeida et al., 2019). Thus, considerable efforts have been made to resolve the above shortcomings by incorporating oxophilic promoter materials such as Ru (Liu et al., 2005, Goel and Basu, 2014 and Hu et al., 2016), Sn (Jiang et al., 2010 and López-Suárez et al., 2015), Rh (Silva-Junior et al., 2013 and Wang et al., 2017), Pd (Kadirgan et al., 2009 and Long et al., 2011), Mo (Wang et al.,

2007 and Pech-Rodríguez et al., 2017) and Ni (Soundararajan et al., 2012 and Mathe et al., 2014) into the platinum crystalline structure to form bi-metallic electrocatalysts with improved electrocatalytic activity in bi-metallic alloys over the last few years. Among all the bi-metallic electrocatalysts, Pt-Sn and Pt-Ru are the most promising anode material for ethanol electrooxidation in the acidic medium due to their improved ability to overcome CO poisoning with enhanced electrocatalytic activity. Improving the catalytic activity of bi-metallic electrocatalysts is often interpreted by a bi-functional mechanism and/or by ligand/electronic effects (Datta et al., 2009, Velázquez-Palenzuela et al., 2010, Garcı´a et al., 2012, Muthuswamy et al., 2013 and Gu et al., 2018). The enhancement of the catalytic activity of bimetallic electrocatalysts is explained by many positive aspects, such as the extent of the nearest surrounding metal atoms, the interatomic gap in M-M, the vacancy in d bands, and the metal content on the surface. In addition, the structure of metals and their geometry also play a significant role in improving the activity and stability of electrocatalysts. Geometric effects include catalytic morphology (dispersion and size distributions), coordination environment, inter-atomic distance and lattice strain (Dutta et al., 2017).

Tri-metallic alloy electrocatalysts have also been widely studied over the past few years to boost the activity and selectivity of the ethanol oxidation reaction (EOR) against CO_2 generation. Tri-metallic alloy electrocatalysts such as PtRuSn (Chu and Shul, 2010 and Cunha et al., 2011), PtRuMo (Wang et al., 2007), PtRuRh (Nakagawa et al., 2012), PtRuNi (Sudachom et al., 2017), PtSnRu (Antolini et al., 2007), PtSnMo (Lee et al., 2011), PtSnIr (Ribeiro et al., 2007, Tayal et al., 2011 and Ramos et al., 2012), PtSnW (Ribeiro et al., 2008), PtSnCe (De Souza et al., 2011), PtSnNi (Beyhan et al., 2013 and Beyhan et al., 2014), PtSnRe (Tayal et al., 2012) have been investigated for use in direct

ethanol fuel cell (DEFC) as an anode material for ethanol electrooxidation. Open literature states that all tri-metallic electrocatalysts demonstrate enhanced ethanol electrooxidation behavior relative to corresponding bi-metallic Pt-Ru and Pt-Sn electrocatalysts.

The behavior and stability of electrocatalysts for splitting ethanol molecules are heavily dependent on particle size, particle size distribution, and electrocatalyst nanoparticles being distributed on the surface of the support material used (Gu et al., 2018). In the synthesis and performance of electrocatalysts, the support material plays a vital role because it improves the dispersion of active metal nanoparticles by providing a large surface area and provides an effective porous conductive network that enables electron conduction and better diffusion of reactants to reaction sites. The use of electrocatalyst support also has been acknowledged as an effective approach to lowering the use of noble metal particles (Goel and Basu, 2014 and Samad et al., 2018). Supporting material has a major effect on the electrocatalytic activity as it can change the morphology of supported nanoparticles (NPs) and serve as a promoter of the reaction. Highly conductive black carbon with a large surface area, along with its graphite properties, is the most commonly used electrocatalyst support material in low-temperature fuel cells to ensure a large electrochemical reaction surface. Electrically conductive nano-structured carbonaceous materials or carbon black provides a network for the conductivity of electrons in electrode (anode and cathode) layers with very low ohm resistance (Goel and Basu, 2014, Rizo et al., 2017a and Samad et al., 2018). The Vulcan XC-72 is the most commonly used support material, considering its physical properties, among all carbon support materials. However, Vulcan XC-72 comprises around 30 % of the total S_{BET} region with micropores of less than 1 nm, comprising a significant portion of active electrocatalyst nanoparticles

that may not be accessible to reactants and thus, remain unutilized (Lazaro et al., 2011 and Calvillo et al., 2011). In addition, the Vulcan XC-72 is very costly and not readily available. For all these reasons, carbon support material like acetylene black, which is cheaper and easily available and highly nanostructure could be treated as suitable support material for the synthesis of bi-metallic electrocatalyst for ethanol electrooxidation. Over the last decades, a variety of novel non-conventional carbonaceous support materials like mesoporous carbon (Calvillo et al., 2007 and Salgado et al., 2010), carbon nanofibres (Rizo et al., 2017a and Rizo et al., 2017b), carbon nanotubes (CNTs) (Jha et al., 2011, Goel and Basu, 2014, Sudachom et al., 2017 and Romero-Cano et al., 2019) and graphene (Jha et al., 2011 and Shen et al., 2015) also have been studied. In particular, CNTs and graphene are expected to be suitable support materials in low-temperature fuel cells for anode electrocatalysts, as they have high surface area, high electrical conductivity and excellent chemical stability.

Surface functionalization of electrocatalyst support materials is typically carried out to facilitate homogeneously oxygenated surface functional groups and binding sites in order to obtain highly scattered metallic nanoparticles with size-controllable loading on the surface of the support material. The particle size, morphology, size distribution, stability, and dispersion of metal nanoparticles on the support surface are greatly affected by the pretreatment of support material and preparation procedure of electrocatalyst synthesis. The chemical functionalization of carbon support through HNO_3, HNO_3-H_2SO_4 or H_2O_2 results in defective and functionalized groups such as hydroxyl (–OH), carboxyl (–COOH) and carbonyl (>C=O) on the surface of the support material (de La Fuente et al., 2009, Asgardi et al., 2015 and Rizo et al., 2017a). In addition, these generated oxygenated

surface species also improve the hydrophilic nature of the support and enhance the diffusion of the reagents to the active sites.

The electrocatalyst synthesis method can significantly influence the composition, morphology and dispersion of metal nanoparticles and their electrocatalytic performance. Generally, carbon-supported electrocatalysts are synthesized by impregnation, colloidal, and microemulsion methods (Liu et al., 2005 and Esmaeilifar et al., 2010). The polyol reduction method (PLM) is one of the most efficient electrocatalyst synthesis techniques in which a polyol such as ethylene glycol acts as both a solvent and a reduction agent for metallic precursors. Recently, the polyol reduction approach has gained attention as it offers precise size control and well-dispersed metal nanoparticles over the support material without using any external stabilizers. In this process, glycolate produced from ethylene glycol oxidation in an alkaline medium stabilizes metal colloids (Bock et al., 2004 and Wang et al., 2011). Similarly, the formic acid reduction method (FAM) has become very popular for the synthesis of fuel cell electrocatalysts. Thus, electrocatalyst synthesis using different methods and finding the most appropriate one in terms of their activity would help to develop high performance DEFC.

It is seen from the published literature that the detailed study on synthesis and characterization of different types of bi-metallic and tri-metallic electrocatalyst followed by application in single cell DEFC is missing. Most of the research works are reported either on DEFC using commercial electrocatalyst (Pramanik and Basu, 2007, Pramanik et al., 2008 and Gupta and Pramanik, 2019) or synthesized electrocatalyst for ethanol electrooxidation in half cell (García et al., 2012, Beyhan et al., 2014, Corradini et al., 2015, Hu et al., 2016 and Themsirimongkon et al., 2018) only. In some cases,

electrocatalysts have been synthesized and characterized without detailed studies in single cell DEFC.

Thus, in this thesis, a thorough studies were performed on the synthesis and characterization of Pt-based bi-metallic and tri-metallic anode electrocatalysts supported on low cost functionalized acetylene black (C_{PAB}) and functionalized multi-walled carbon nanotubes (f-MWCNT) using different synthesis methods such as PLM and FAM for ethanol electrooxidation. The laboratory synthesized electrocatalysts were used in DEFC to evaluate the performance of electrocatalyst after manufacturing the membrane electrode assembly (MEA) which is the heart of the fuel cell. The optimum conditions of different parameters e.g., ethanol concentration, loading of the anode and cathode electrocatalyst, electrocatalyst types and cell temperature were investigated in order to achieve the maximum output in terms of power density with low overpotential from a DEFC using the fabricated electrodes.

The thesis chapters are listed in a brief overview below. **Chapter 1** explains general introduction to the energy scenario, the basic concept of the fuel cell, ethanol as fuel along with its advantages over methanol, anode electrocatalysts, supporting materials and electrocatalyst synthesis methods. The detailed of the literature review and specific objectives of the thesis are given in **Chapter 2**. **Chapter 3** explains the materials used in the experiment and the experimental details related to the formulation of anode electrocatalysts such as the functionalization of supporting materials, the synthesis of supported nano-electrocatalysts, fabrication of working electrodes cyclic voltammetry and chronoamperometry for electrochemical measurements, the manufacture of anode, cathode and membrane electrode assembly, the fabrication of single cell set-up to evaluate cell performance are discussed. **Chapter 4** provides description of the surface

response methodology technique that was used to optimize the DEFC process parameters and validated with experimental data for the same process parameter of actual DEFC set-up. **Chapter 5** presents the important findings and discussions on physicochemical characterization of synthesized electrocatalysts, surface morphology, crystal structure, particle size and dispersion of the metal nano-particles on the supporting materials. The electrochemical characterization of synthesized electrocatalysts using cyclic voltammetry and chronoamperometry is also discussed. The experimental results of a manufactured DEFC using synthesized electrocatalysts as an anode material are also discussed in this chapter. Finally, **Chapter 6** summarizes the main findings and discussions of the overall studies. Some significant suggestions for further work in this field are discussed in the section future scope. At the end of the thesis, the appendices and the references are given.