CHAPTER 1

INTRODUCTION

In recent decades, economic development has led to substantial growth in global energy consumption. The world's global energy requirement is increasing day by day due to the exponential population growth across the globe (Azad et al., 2019), followed by modern civilization's growth, change of lifestyle, daily activity based on electronic devices, rapid increase of automobiles uses, and fast industrialization. The global energy requirements are mainly fulfilled by conventional sources of energy which is derived from fossil fuels like coal, petroleum, and natural gas. Generally, two forms of energy i.e., thermal and electrical energy are wildly used around the world. The electrical energy production in India reported by central electricity authority (CEA), government of India shows that among all conventional sources of energy coal is used in highest amount for electricity generation (55.42 %) than natural gas (6.74 %) and petroleum (0.0014 %). The other sources of energy are renewable (35.85 %) and nuclear energy (1.83 %) (CEA, 2020). It is well known that the fossil fuel consumption is more for electricity generation. However, fossil fuel reserves are limited and it is also the leading cause of air pollution and global warming by releasing harmful gases such as CO_2, SO_x and $NO_{x,}$ etc. Moreover, nuclear energy is hazardous to human health as the nuclear plant releases radioactive material into the environment (Mellawati, 2019). Thus, the world scientists and researchers are searching for an alternative energy source that is cost competitive with fossil fuels, readily available to the mass people and environmentally sustainable. The alternative sources of energy are nonconventional or renewable energy like solar energy, wind energy, and biomass energy which are used in major amount. However, these energy sources have some limitations and drawbacks. The solar energy is weather

dependent. The cloudy and rainy days effect on the energy production system. The initial installation cost of solar plant is very high. Moreover, solar panel takes lots of space and the storage of solar energy i.e., battery technology is very expensive. The drawbacks of wind energy generation are, it requires steady wind velocity and works on selected places such as sea shore and valley. The major drawback of biomass is moisture content which creates problem in pre-treatment and biomass conversion processes. It also contains alkaline and halogen elements which creates formation of many dangerous chemicals such as Cl_2, HCl, HBr and HF. It also enhances fine particulate emissions and water soluble fraction (Vassilev et al., 2015). The hazardous trace elements in biomass volatilized which causes air pollution and water soluble elements might cause water pollution during the conversion process (Vassilev et al., 2015).

In this perspective fuel cell has drawn more attention for the generation of electricity via electrochemical conversion of fuel like hydrogen and hydrogen rich molecules such as methanol, ethanol and glycerol, and oxidants oxygen from air or pure oxygen. The fuel cells have many advantages such as environment friendly, higher energy efficiency and minimal emissions of poisonous species. The fuel cell was invented as energy conversion device in 1839, middle of 19^{th} century by Sir William Robert Grove who was a lawyer and scientist (Larminie and Dicks 2003). However, the concept was initially given by Christian Friedrich Schönbein (Carrette et al., 2001). Their joint efforts for the development of fuel cell and contribution for such innovation shall always be remembered.

Figure 1.1 shows a schematic of hydrogen/oxygen fuel cell where H_2 gas as fuel enters at the anode and splits into proton and electron. The proton passes through the electrolyte membrane and electron through the external circuit and reaches cathode side. At cathode side, electrons and protons reacts with O_2 gas and generates electricity. The fuel cell also

and produces water and heat as byproduct. Fuel cells are more efficient than heat engines (Bagotsky, 2009; Badwal and Foger 1996) with an energy efficiency estimate of 40-50 % in electric power and 80-85 % in total energy (Leger and Coutanceau 2008).

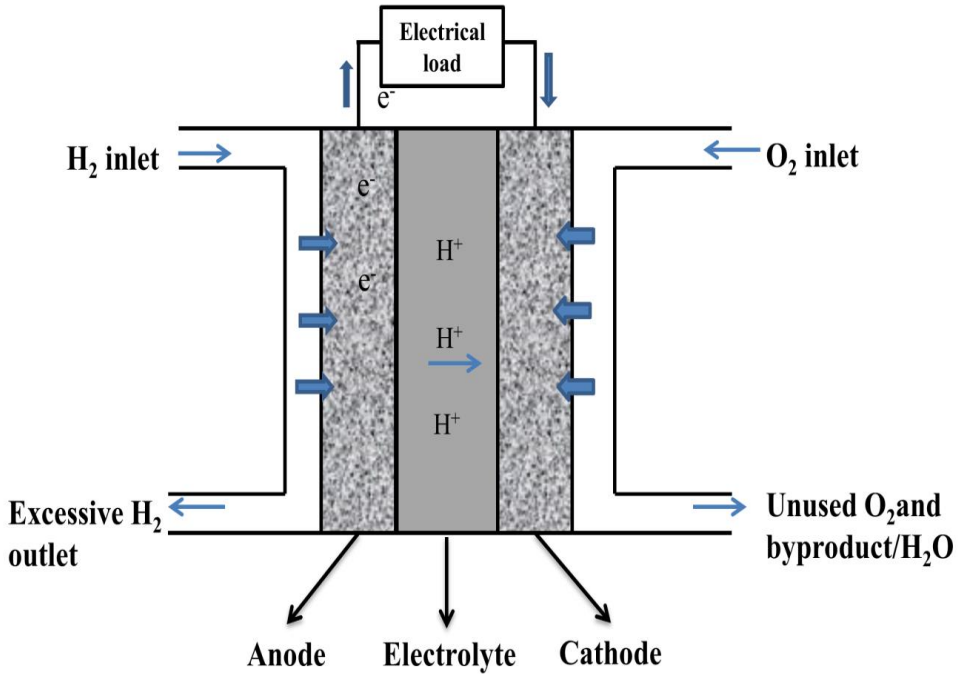


Figure 1.1 Schematic of a hydrogen/oxygen fuel cell with proton and electron transport.

The high power generation in the fuel cell depends on the faster electrochemical reactions at the electrode surface (Hayre et al., 2009) that makes the electrocatalyst selection a very important criterion for fuel cell design. Fuel cells do not generate harmful gases, it has no moving parts and operate silently and smoothly. The maintenance cost of the fuel cell is also low (Pagano and Piegari 2002).

Inspite of several advantages of fuel cells, further development work on fuel cell was stopped at the beginning of 20th century due to high cost of unit energy production, expensive fuel cell components like Pt based electrocatalysts, costly proton exchange membrane and high loading of electrocatalyst required at the primary stage of fuel cell research.

However, owing to the increase in electricity consumption due to industrialization and increase in human population, the conversion of chemical energy into electrical energy became more important at the beginning of the 20th century (Carrette et al., 2001). Thus, the development work on fuel cell again gained momentum with some break through research and development work in the area of fuel cell such as development of highly conducting proton exchange membrane Nafion® by Dupont (USA) and synthesis of high surface area highly active anode and cathode electrocatalyst using novel methods improved the cell performance dramatically even at low loading of electrocatalysts. Thereby, cost of energy production from fuel cell got reduced. However, there are many drawbacks of conventional fuel cell using membrane electrolyte. The conduction of ions through membrane electrolyte get reduced at high temperature due to dehydration of membrane. The flooding of cathode, anode dry out and fuel crossover through electrolyte also results in low performance of fuel cell.

Thus, the problem associated with membrane in fuel cell and other issues can be eliminated using an alternative of conventional fuel cell which is known as membraneless microfluidic fuel cell. The membraneless microfluidic fuel cell is achieved by maintaining the laminar flow with low Reynolds number of anode and cathode streams through the microchannel of size < 1mm (Kjeang et al., 2009) (Figure 1.2). This microfluidic fuel cell (MFC) is miniaturised form of fuel cell. The miniaturization of fuel cell device deals with several advantages over conventional membrane electrolyte based fuel cells such as portability, faster mass transfer at the electrode and higher power density (Shaegh et al., 2011).

The microfluidic fuel cell (MFC) device offers an opportunity to reduce the problems related with the use of PEM or anion exchange membranes in the fuel cell. The MFC technology removes or eliminates the use of a physical membrane by developing laminar

flow of the streams which helps to form inter diffusion layer between the fuel and oxidant streams (Ferrigno et al., 2002; Kjeang et al., 2009).

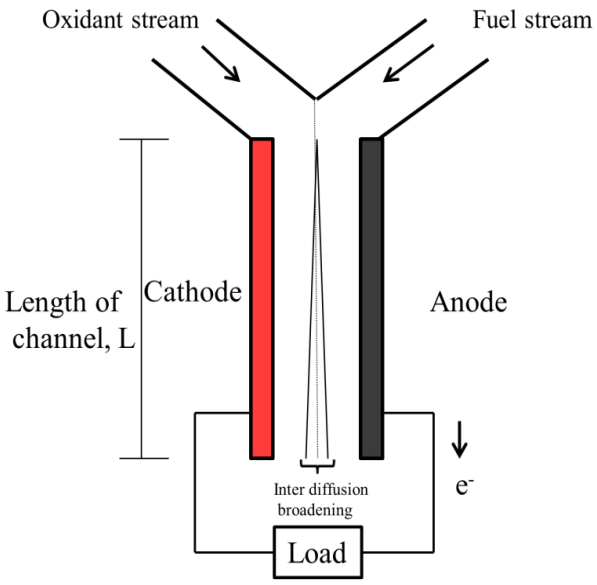


Figure 1.2 Schematic of microfluidic fuel cell.

The parallel and co-laminar flow of two streams of fuel and oxidant and low Reynolds numbers (less than 1 and upto 100), where viscous forces lead over inertial force and the surface forces are more relevant than the body forces (Banerjee et al., 2019). The interface of two streams acts as virtual membrane for the transport of ions. The electrons generated at anode side passed through the external circuit and reached at cathode side to complete the cathode reactions.

The MFC device can be fabricated and constructed using low cost microfabrication and micromachining methods e.g., photolithography, soft lithography laser etching and CNC machine (Fiorini and Chiu 2005; Panjiara and Pramanik 2020a). The application areas of this MFC are mainly low power consuming devices like camcorder, cell phone, laptop, glucose sensor, and pacemaker etc. (Pramanik and Rathoure 2017).

The first microfluidic fuel cell was reported in 2002 by Ferrigno et al., and there after several studies have been reported on cell architectures i.e., the shape of the microchannel, geometry of electrodes and positioning of electrodes with varying flow rates of anode and cathode streams. A very comprehensive study by Kjeang et al., (2009) and Shaegh et al., (2011) in the field of MFCs have triggered the research and development in this area over the past few years to enhance the cell performance. The performance of MFC under load (current $i > 0$) depends on the activation loss, ohmic loss and mass transfer loss. The activation loss is mainly associated with the electrocatalyst properties, nature of electrocatalyst and cell temperature (Bard and Faulkner 2002). The ohmic loss is associated with the electrode spacing, electrolyte concentration and various interconnections (Shaegh et al., 2011). Whereas, the mass transfer loss occurs due to the electrode architecture and channel geometry, fuel and oxidation concentration, diffusion mass transfer and replenishment rate of depleted boundary layer. Thus, these are the important factor to be considered to obtain maximum cell performance form the MFC device. As the cell architecture and design play an important role to improve MFC performance, thus many type of MFC design e.g., Y-shaped (Jindal et al., 2017), T-shaped (Kjeang et al., 2008), I-shaped (Togo et al., 2007) and F-shaped air breathing (Jayashree et al., 2006) have been reported in open literature till date. Among all design air breathing MFC is found to be better than the other type of design/cell architecture. The oxidant used is generally oxygen from atmospheric air (Rathoure and Pramanik 2016). The reason for using atmospheric oxygen as oxidant is the diffusivity of oxygen from atmospheric air is higher than the dissolved oxygen in cathode electrolyte stream. Due to this fact, the air breathing cathode enhances the cell performance and fuel utilization (Jayashree et al., 2005). Thus, in the present thesis work, laboratory fabricated air

breathing microfluidic fuel cell of Y-shaped and T-shaped were considered to enhance the cathode mass transfer and simultaneous reaction.

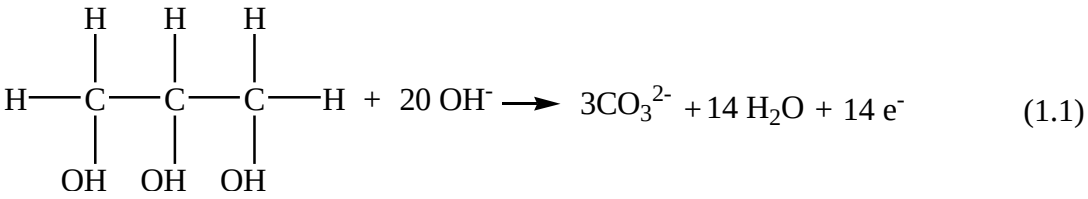
There are different types of fuel and oxidants are studied in the MFC device to get the maximum power density from the cell. The commonly used fuels in MFC are methanol (Rathoure and Pramanik 2016), ethanol (Armenta et al., 2016), ethylene glycol (Coronel et al., 2019), glycerol (Dector et al., 2013a), formic acid (Zuria et al., 2014), vanadium (Farrigno et al., 2002) and glucose (Galindo et al., 2014). The oxidants used in MFC are hydrogen peroxide (Rathoure and Pramanik 2016; Yan et al., 2018), potassium permanganate (Liu et al., 2019), sodium hypochlorite (Martins et al., 2018b) and atmospheric oxygen (Maya-Cornejo et al., 2016; Rathoure and Pramanik 2017). Among all fuels, lower aliphatic alcohols like methanol and ethanol are very popular. However, they have certain merits and demerits. Methanol is low molecular weight compound, simplest alcohol without having any C-C bond in its molecular structure and thus, easy to breakdown using the present Pt based electrocatalyst resulting in very high current and power density in comparison to any other alcohols. However, methanol is not primarily alcohol and it is produced via complex route of Fischer-Tropsch reaction (Santos and Alencar 2019). Moreover, methanol is neuro-toxic and low boiling point alcohol (Barceloux et al., 2002). Thus, methanol based MFC is difficult to operate at higher temperature (65 ^{o}C). Ethanol is non-toxic and it can be produced from sugar containing biomass by fermentation. However, the C-C bond breakage of ethanol for complete electrooxidation to CO_2 is difficult (Antolini, 2007). The electrooxidation of ethanol results in the formation of intermediate products such as acetaldehyde, acetic acid and acetate (Simoes et al., 2010). Thus, the current and voltage produced are low for ethanol based MFC.

On the other side, glycerol has drawn much attention at the present time due to its several advantages like glycerol is non-volatile, non-toxic as well as non-flammable which makes it favourable to use as eco-friendly fuel for fuel cell device (Schell et al., 1996; Faro et al., 2011; Panjiara and Pramanik 2021b). Glycerol also shows comparable energy density (5.0 kwh kg^{-1}) to that of methanol (6.1 kwh kg^{-1}), ethanol (8 kwh kg^{-1}) and ethylene glycol (5.2 kwh kg^{-1}) (Ilie et al., 2011). Moreover, it is a byproduct of biodiesel manufacturing via transesterification of vegetable oils and available in large quantity (Jazie et al., 2013), also have low market prices and non-hazardous (Panjiara and Pramanik 2020a; Guima et al., 2020). Thus, glycerol was selected as the most promising fuel for the present study in an especially laboratory designed Y-shaped and T-shaped air breathing microfluidic fuel cell to produce low cost electrical power.

The electrocatalyst plays an important role in splitting fuel molecules into electrons and ions via electrochemical dissociation at the anode of a fuel cell. Most of the electrooxidation of alcohols have been focused on platinum or palladium based electrocatalysts, probably due to their excellent electrocatalytic behaviour (Antolini and Gonzalez 2010). Thorough literature survey shows that palladium (Pd) is the most active metal electrocatalyst for glycerol electrooxidation over any other noble metal electrocatalyst (Simoes et al., 2011; Houache et al., 2019). The kinetics of alcohol electrooxidation is very much dependent upon the electrolyte medium. The electrooxidation of alcohols reactions are carried out either in acidic or alkaline medium (Ma et al., 2012). However, the alcohols electrooxidation reaction kinetics is faster in alkaline medium than acidic medium (Wang et al., 2003). It is also seen that, palladium based electrocatalysts are most active for electrooxidation of glycerol in alkaline medium (Bianchini and Shen 2009). It should be noted that glycerol molecule has C-C bonds in the molecular structure which is quite difficult breakdown using present platinum based

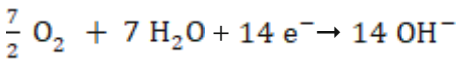
electrocatalysts. The complete electrooxidation of glycerol ends with the formation of carbonate in alkaline media and 14 electrons which reacts with oxygen and water molecules to generate 14 OH^- ions as shown in the following Equation (1.1) and Equation (1.2) (Simoes et al., 2010).

Anode reaction:



(1.1)

Cathode reaction:



(1.2)

Although, Pd is suitable and electrochemically active electrocatalyst for glycerol, Pd based bimetallic electrocatalysts are not available commercially in the open market. Generally, synthesized single metal Pd based electrocatalyst is used for glycerol electrooxidation in microfluidic fuel cell (Dector et al., 2013a). Thus, there is an urgent need to synthesized a new combination of bimetallic Pd-M (where M is Pt, Ni etc.) electrocatalysts to improve the electrooxidation kinetics and activity via a suitable reaction pathway which allows to split the C-C bond of glycerol at low activation energy (Benipal et al., 2017). The role of palladium in bimetallic electrocatalyst is to reduce the poisoning of electrode by minimizing the CO build up on electrocatalyst surface (Grace et al., 2006).

Thus, in this thesis work a thorough study is carried out on the synthesis and characterization of low cost palladium based bimetallic anode electrocatalysts for glycerol electrooxidation. The performance of the synthesized electrocatalysts are evaluated in laboratory fabricated Y-shaped and T-shaped air breathing microfluidic fuel cell to enhance the mass transfer of oxygen at cathode followed by oxygen reduction reaction. The half cell analyses of the developed anode using synthesized Pd based electrocatalyst were also studied for the electrochemical characterization of electrodes. All experiments are performed in alkaline medium with different operating parameters such as electrocatalyst type, electrocatalyst loading, fuel concentration, electrolyte concentration, oxidant type and cell temperature in the single cell. The next thesis chapters are described below in brief.

The present electricity production scenario and its drawbacks with the alternative source to fulfill the present requirements using MFC technology are discussed thoroughly in the Introduction (**Chapter 1)**. The **Chapter 2** comprises of the detailed literature reviews research gap and specific objectives of the thesis. **Chapter 3** describes the material used throughout the experiment and experimental details related to the development of glycerol based air breathing microfluidic fuel cell, fabrication of Y-shaped and T-shaped air breathing microfluidic fuel cell, synthesis of anode electrocatalyst, physicochemical and electrochemical characterization of electrocatalyst, fabrication electrode and single cell performance. **Chapter 4** deals with the optimization of operating parameters and validation using response surface methodology for the best combination of electrocatalyst and best design of air breathing microfluidic fuel cell. **Chapter 5** deals with result and discussion based on the physicochemical characterization of electrocatalyst using X-rays diffraction (XRD), Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Transmission electron microscopy (TEM) whereas,

electrochemical characterization were performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results on single MFC studies are discussed using polarization and power density curves. Process parameters are optimized using RSM and results are discussed thoroughly. The dimensionless numbers, efficiency of MFC, and stability test of MFC were also discussed at the end of the **Chapter 5**. Finally, **Chapter 6** summarizes the essential conclusions and discussions of the thesis, and some important recommendation for the further work in this area. The appendices and references are presented at the end of the thesis.