CHAPTER -1

INTRODUCTION

A continuously growing demand for miniaturized power sources for portable electronic telecommunication and computing devices such as mobile phones, laptop computers, and biomedical appliances has promoted research and development activities in the area of microfluidic fuel cell technology. In developing countries, access to affordable and reliable energy services is a basic need for reducing poverty and improving health, increasing productivity, enhancing competitiveness and promoting economic growth. The growth in world energy demand in the coming decades will be very high. The world energy consumption is projected to increase by 28 % from 2015 to 2040, according to the international energy outlook 2017 (IEO 2017). Most of this growth is expected to come from countries where demand is driven by strong economic growth, which includes China and India, accounts for more than 60 % of the world's total increase in energy consumption from 2015 to 2040. World energy consumption from all fuel sources, except for coal will be increased through 2040. Renewable fuels sources are expected to be the fastest growing energy source with consumption growing by an average 2.3 % per year between 2015 to 2040 (IEO 2017).

The energy demand is met by primary sources of energy like fossil fuels such as natural gas, petroleum oil, and coal and to a lesser extent, nuclear by fission of radioactive elements, indirect solar heating and photovoltaic cells, hydroelectricity, wind, geothermal and biomass. However, about 75% of the today's energy demand is fulfilled by fossil fuels.

Fossil fuels generate energy by combustion and produce pollutants, e.g., oxides of sulfur, nitrogen, carbon and unburned hydrocarbons, which are introduced into the atmosphere resulting in a large number of problems to the environment (IPCC 2007 and Stern 2007). The environmental issues, depletion of fossil fuels and cost of fossil fuel coupled with low production rate compared to the demand are the reason to design and develop eco-friendly, compact and modular power generator, which is economically viable. Currently, fuel cells are found to be very promising energy generating devices for the stationary and mobile applications with significant environmental advantages (Veziroglu 1987, Veziroglu 1998, Muradov et al., 2005).

Fuel cells are the device that converts the chemical energy of supplied fuel into electrical energy and heat by oxidation and reduction reactions in the presence of electrocatalyst. Fuel cells consist of an electrolyte medium sandwiched between anode and cathode (fig 1.1).
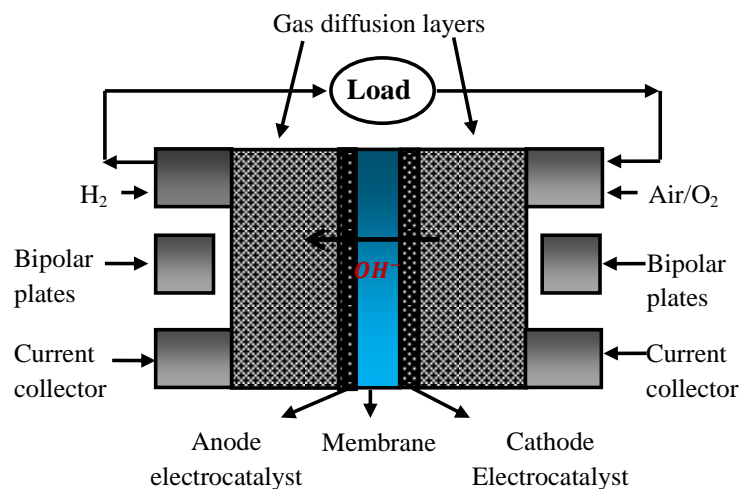

Figure 1.1 Schematic of a hydrogen-oxygen anion exchange membrane fuel cell

Fuel is delivered to the anode side, and the oxidant is delivered to the cathode side. Ions generated as a result of electrooxidation or reduction reactions are transported from one electrode to the other through the ionically conductive electrolyte. The electrolyte may be acidic or alkaline in nature for acidic electrolyte (e.g., Nafion$^{®}$) protons or H^+ ions move from anode to cathode side, and alkaline electrolyte allows OH^- moving from cathode to anode side. The electrons generated at the anode transferred to the cathode through the external circuit, and hence the electricity is generated. The fuel and oxidant streams do not mix with each other at any point in the fuel cell, and no actual combustion occurs as in combustion engines. Fuel cells, unlike conventional thermal power plants, are not operating on a thermal cycle and thus, they are not limited by the Carnot efficiency. A fuel cell has a high potential in replacing conventional combustion engines running on the fossil fuels.

The first working prototype fuel cell was developed by a Welsh scientist, Sir William Robert Grove, a judge and an amateur scientist. He conducted the first known demonstration of the fuel cell in 1839. Nowadays researcher has developed a wide variety of fuel design for power generation which is practical for widespread applications regarding cost, efficiency, and reliability (Perry et al., 2002). These various configurations are classified in many different ways in the literature (Srinivasan et al., 2006). Fuel cells are primarily classified according to the materials utilized for the electrolyte, fuel used and regarding the operating temperature range. In this context, low-temperature fuel cells based on proton exchange membrane (PEM) technology are found very promising energy generating devices for smaller electronic devices (Pramanik et al., 2007). The PEM fuel cell uses gaseous hydrogen as fuel and oxygen or air as an oxidant. At the anode, hydrogen molecules are splitted into protons and electrons. These protons travel through the proton

conducting membrane, and electrons from the external circuit toward the cathode. On the cathode, oxygen molecules react with the electrons and protons. Heat and water produced as a byproduct. However, membranes electrolyte (e.g., Nafion$^{®}$) offers a certain amount of ohmic polarization and allows fuel crossover, both of which lower the fuel cell performance. The use of membranes requires complex water and thermal management strategies to enable high charge transfer rates. All these problems have propelled to develop a low cost miniaturized fuel cell which eliminates the use of static physical barrier (membrane) termed as the membraneless microfluidic fuel cell (Shaegh et al., 2012).

A microfluidic fuel cell (MFC) is defined as a device that incorporates all fundamental components of a fuel cell within a single microchannel (channel width <1000 μm) and its walls. Usually, microchannels are defined as channels with a characteristic dimension less than 1 mm and greater than 1 μm (Sharp et al., 2002), and the fluid manipulation inside the microchannels is known as microfluidics. Since its invention in 2002, microfluidic fuel cell technology has developed rapidly and is now considered a candidate for commercial small-scale portable power generation (Bazylak et al., 2005 and Chang et al., 2006). The most common configurations rely on the laminar nature of flow in microstructures to maintain sufficient separation of fuel and oxidant streams, flowing side-by-side in a co-laminar format. The fuel and oxidant are fed in parallel micro-channels, and the liquid-liquid interface produced allows for proton diffusion, avoiding the need for polymeric membrane (fig 1.2). Supporting electrolyte contained in both co-laminar streams facilitates ionic conduction between the electrodes. Mixing by diffusion is restricted to an interfacial width at the center of the channel, depending on mean velocity and channel geometry. The electrode spacing is typically an order of magnitude larger than the interdiffusion width.

Microfluidic fuel cells have several advantages as compared to traditional proton exchange membrane (PEM) based fuel cells. The benefits are (i) fuel and oxidant streams may be combined in a single microchannel (ii) fuel and/or oxidant crossover can be minimized by adjusting the flow rate of the co-laminar streams (iii) no ion exchange membrane is required (iv) sealing, manifolding, and fluid delivery infrastructure requirements are reduced and (v) issues related to membrane hydration and water management are eliminated. In addition, microfluidic fuel cells may be manufactured using inexpensive micro fabrication methods and low-cost materials. There are many designs of microfluidic fuel cells are available in the open literature, e.g., Y-shape, T-shape, F-shape with air breathing cathode, etc.
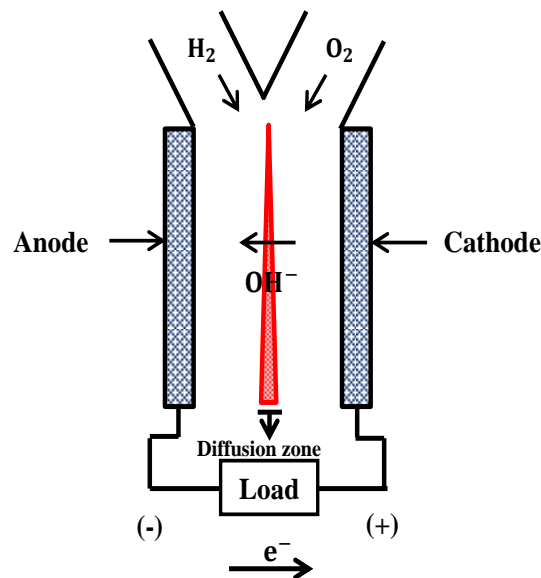

Figure 1.2 Y-shape microfluidic fuel cell design.

Several different fuels have been employed in microfluidic fuel cells presented to date. These include hydrogen (Shukla et al., 2005 and Erickson 2005), methanol (Qian at al.,

2006 and Logan et al., 2006), vanadium redox species (Ferrigno et al., 2002 and Kjeang et al., 2007), formic acid   (Choban et al., 2004 and Chang et al., 2006), glucose (Cuevas-Muniz et al., 2011) and ethanol (Pramanik et al., 2015). Among all these fuels, methanol, ethanol, and $NaBH_4$ are considered as promising fuels. Methanol is widely used as fuels in direct methanol fuel cells for mobile applications such as electric vehicles (Lamy et al., 2001) laptop, camcorder, etc. Methanol is readily available, cheaper in price, and it can be easily stored as a liquid. Methanol is synthesized from natural gas via its incomplete combustion to produce synthesis gas. Methanol is generated via catalytic conversion of synthesis gas. Methanol has high energy density (6.09 KWh/kg) which is comparable with other aliphatic alcohols, very smooth electrooxidation on Pt-Ru/C and it is a liquid fuel thus, no leakage problem like H_2 gas is present. However, methanol has some disadvantages, i.e., it is toxic, has a low boiling point (65 ^{o}C), it is not a primary fuel, and anode poisoning by strongly adsorbed intermediate (mainly CO) formed during methanol oxidation.

Therefore, other aliphatic alcohols such as ethanol could be a good choice as an anode fuel in low temperature fuel cells. It is attractive fuel because of its low toxicity and high theoretical energy density (8.0 kW h kg^{-1}) (Lamy et al., 2002, Xu et al., 2011, Song et al., 2007, Zhang et al., 2013 and Karim-Nezhad et al., 2012). It is seen that the complete oxidation of ethanol to CO_2 is severe due to the difficulties in C–C bond breaking and the formation of CO intermediates that poison the platinum anode electrocatalysts (Lamy et al., 2004, Tayal et al., 2011 and Tayal et al., 2012). It implies platinum alone is not a good electrocatalyst for ethanol electrooxidation and among others, Pt-Ru, Pt-Sn, and Pt-Ru-Sn alloys have been considered and tested as suitable electrocatalyst materials (Goel et al.,

2012, Tayal et al., 2012 Jayashree et al., 2009, and Lamy et al., 2001). It is seen that ethanol is renewal in nature as it can be produced from sugar containing agricultural biomass resources (Pramanik at al., 2007). Moreover, ethanol has been used as fuel in PEM based direct alcohol fuel cell (Pramanik et al., 2007). However, no such literature is available apart from methanol and ethanol on direct use of ethanol as fuel in an air breathing microfluidic fuel cell.

Hydrogen is considered as a clean energy carrier because the fuel cell system and combustion process both produce energy and by-product water only. Moreover, hydrogen gas has a high energy density (39.4 kWh/kg) than hydrocarbons and other fuels. However, the hydrogen gas has many disadvantages, e.g., economical production of pure hydrogen gas and onboard storage, safety issues related to the hydrogen gas as it is highly explosive and low power output per unit weight of fuel cell and processor together (Ioannides et al., 2000 and Pramanik et al., 2011). These drawbacks of hydrogen gas have propelled the researchers to work on alternate fuel, e.g., NH_3, N_2H_4 and $NaBH_4$ for direct feeding in the fuel cell in place of pure hydrogen gas (Lee et al., 2002 and Maffei et al., 2005). Among all these fuels, sodium borohydride ($NaBH_4$) has attracted much attention as potential hydrogen storage media due to high hydrogen capacity (10.6 wt %) (Lee et al., 2012). It can be stored in the liquid phase, and also it is a stable nonflammable in alkaline medium. $NaBH_4$ is also renewable and environmentally friendly fuel. Also, the use of hydrogen-rich compound $NaBH_4$ in fuel cell could eliminate the storage and transportation problem. The production rate of hydrogen is easily controlled, and pure hydrogen can be obtained by hydrolysis of $NaBH_4$ as shown below (equation 1.1) (Schlesinger et al., 1953)

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad\qquad (1.1)$$

It is seen in equation (1.1) that hydrogen is the only gaseous product of the reaction. The hydrogen gas can be obtained from the above reaction after separating the borate, which can be recycled into sodium borohydride again. Hydrolysis of sodium borohydride is an exothermic reaction, so this reaction does not require any additional heat supply and can take place at room temperature (Lee et al., 2012).

The theoretical open circuit voltage (OCV) for microfluidic fuel cell using methanol, ethanol and sodium borohydride as fuel and oxygen as the oxidant, as calculated from Gibbs free energy are 1.213 V, 1.145 V and 1.64 V, respectively (at standard conditions of anode and cathode i.e., 1.01 bar and 25 ^{o}C). The energy efficiency[*] (ε_r) of methanol-oxygen, ethanol-oxygen and sodium borohydride-oxygen fuel cell under reversible conditions (25 ^{o}C and 1.01 bar) are 96.7, 97.0 (Lamy et al., 2001) and 91.02 (Elumalai et al., 2014) and much better than that of H$_2$/O$_2$ fuel cell (0.83 at 25 ^{o}C) (Lamy et al., 2001). Therefore, methanol, ethanol and sodium borohydride are very attractive fuel for a low temperature air breathing microfluidic fuel cell.

An air breathing microfluidic fuel cell is still in the developing stage. Not many studies on single air breathing microfluidic fuel cell based on aliphatic alcohols or sodium borohydride are found in the open literature. Investigations on half-cell analysis on noble

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[*] $\varepsilon^r = \frac{-\Delta G}{-\Delta H}$, which is the ratio of the molar Gibbs free energy change, ΔG of methanol, ethanol, or sodium borohydride electrooxidation to the enthalpy change, ΔH, of the reaction, respectively.

and non-noble metal electrocatalyst using different aliphatic alcohols or sodium borohydride mixed with alkaline medium have been reported (Daryakenari et al., 2016). Almost, no work on air breathing stack development is found in open literature and the present research. Although quite possible that the development work on various types of the microfluidic fuel cell is being carried out in different research and development organizations but their detailed studies on various operating parameters are not reported in the present literature to present the intellectual property right. Thus, considerable progress is still warranted regarding design, material developments, and performance. In this thesis, an innovative air breathing microfluidic fuel cell is developed, which uses methanol, ethanol or NaBH$_4$ as fuel in the anode and air/O$_2$ as oxidant at the cathode. The thesis chapters are described below in brief.

General introduction about the energy scenario, basic principle of the microfluidic fuel cell, methanol, ethanol or sodium borohydride as fuel and their benefits are discussed in **Chapter 1. Chapter 2** presents the literature review and specific objectives of the thesis. **Chapter 3** describes the experimental details related to the development of air breathing microfluidic fuel cell, e.g., fabrication of cell, gas diffusion layer preparation, anode and air breathing cathode preparation and properties, half-cell analysis through cyclic voltammetry and cell performance. **Chapter 4** presents the details of the mathematical model development of methanol, ethanol, and sodium borohydride-based air breathing microfluidic fuel cell. In **Chapter 5** results and discussion based on the characterization of anode and cathode regarding their surface morphology and half-cell, analysis are discussed. The experimental results of single cell and model development are also presented in this chapter. Finally, **Chapter 6** summarizes the essential conclusions of the thesis, and some

useful recommendations for further work in this area also showed. The appendices and the

references are provided at the end of the thesis.