

CHAPTER 2

LITERATURE REVIEW AND OBJECTIVES

2.1 Literature Review

In this chapter, literature review on air breathing microfluidic fuel cell using methanol, ethanol and sodium borohydride as fuel is presented. The subject covered is divided into several parts, and they are microfluidic fuel cell type/design, electrode materials, electrolyte, half-cell analysis and cell performance. Based on literature review, the objectives of this thesis are finalized.

2.1.1 Microfluidic Fuel Cell Types/Design

According to the design of the implemented electrodes, a microfluidic fuel cell is categorized into three primary type (i) flow over type (ii) flow through type (iii) microfluidic fuel cell with air breathing cathode. All designs can use alkaline, acidic or mixed media configurations.

In flow over type microfluidic fuel cell, fuel and oxidant streams in the channel come in contact in two configurations (a) side by side streaming with the vertical fuel oxidant interface and (b) vertically layered streaming with the horizontal fuel oxidant interface. For both streaming configurations, two electrodes can be position in top bottom configuration (Li et al., 2007), side walls (Choban et al., 2005), or both electrodes on bottom wall or electrodes positioned in grooved channel or an array of electrodes can be implemented in a channel (Lim et al., 2007). In flow over type configuration, fuel and oxidant concentration

decreases because of consumption of fuel and oxidant via electrooxidation over anode and cathode due to lack of the convective mass transport, fuel and oxidant are not replenished immediately (Shaegh et al., 2010). Microchannels in microfluidic fuel cells are fabricated by mainly rapid prototype techniques, standard photolithography, soft lithography or laser micro machining or poly dimethylsiloxane (PDMS) molding and then sealed to a substrate with electrodes (Kjeang et al., 2007 Kjeang et al., 2008).

In a flow through design, the fuel and oxidant streams pass through a three dimensional porous electrode including the catalytic active area. Due to the effective mass transport through porous three dimensional electrodes, the fuel and oxidant are replenished continuously resulting in a higher rate of fuel utilization and greater power output. Flow through design can provide an approximately constant concentration of reactant over the electrocatalyst layer (Salloum et al., 2008).

Low mass transfer and diffusivity of dissolved oxygen as an oxidant limits the performance of microfluidic fuel cell. Moreover, low concentration of dissolved oxygen cannot provide for sufficient replenishment of depletion layer over the cathode. Overcoming this problem a gas diffusion electrode as the cathode is introduced. This cathode is exposed to a high concentration of oxygen in the air and the diffusivity higher than that in dissolved oxygen liquid oxidants. Gas diffusion electrode mainly made of carbon paper covered by electrocatalyst ink containing platinum back nanoparticles and implemented at the top wall as air breathing cathode (Jayashree et al., 2005 Jayashree et al., 2006, Brushett et al., 2009, Hollinger et al., 2010, Whipple et al., 2009 and Abrego-Martinez et al., 2017 etc.). Based

on the geometry microfluidic fuel cells with air breathing cathode are characterized in T-shape, H-shape, I-shape or F-shape, etc.

2.1.2 Microfluidic Fuel Cell Components

The different microfluidic fuel cell components are discussed in this section.

2.1.2.1 Electrode Materials

The fuel cell electrodes, i.e., anode and cathode play a key role in producing higher current density and cell voltage by improving electrodes kinetics or reaction rates at the respective electrodes. The main component of an electrode is electrocatalyst materials which actively take part in the electrooxidation or reduction processes of the cell. In the following section anode and cathode, electrocatalyst are discussed.

2.1.2.1.1 Anode Electrocatalysts

The anode electrooxidation of fuel electrocatalyst material is one of the essential components of the microfluidic fuel cell for the electrooxidation of fuel. It is desirable that the anode electrocatalyst should provide faster reaction kinetics and complete oxidation of carbonaceous fuel (methanol, or ethanol) to CO₂ and H₂O. Platinum, without any doubt, is the most widely used electrocatalyst. Platinum and its alloys seem to be an excellent choice in acidic solution. However, other metallic alloys with platinum or metals can match its performance in alkaline

medium because of the favorable fuel oxidation in alkaline medium. Different electrode materials Pt (Choban et al., 2005, Brushett et al., 2009), Pt/CP (Abrego-Martinez et al., 2017), Pt-Ru (Choban et al., 2005, Jayashree et al., 2006 and Wang et al., 2016), NiO

(Sung and Choi 2007), are studied for the electrooxidation of methanol as fuel in microfluidic fuel cell. Jayshree et al., (2010) worked on methanol/air microfluidic fuel cell with air breathing cathode. The anode electrocatalyst was Pt/Ru (50:50) with high loading (10 mg/cm^2).

The electrooxidation of ethanol is difficult due to C-C bonding. Many electrocatalysts, Pt-Ru (Brushett et al., 2009), alcohol dehydrogenase enzyme (Moore et al., 2005), Pt black (Priya et al., 2014), Pd/C (Lopez-Rico et al., 2015), Pd-NiO/C (Lopez-Rico et al., 2016), Pd/MWCNT (Armenta-Gonzalez et al., 2016), Pd-Ag/MWCNT (Armenta-Gonzalez et al., 2016) are studied for the electrooxidation of ethanol as fuel in microfluidic fuel cell. Armenta-Gonzalez et al., (2016) investigated with two electrocatalysts based on Pd (Pd/MWCNT and PdAg/MWCNT) were evaluated for ethanol electrooxidation in an air breathing microfluidic fuel cell in alkaline medium. Commercial electrocatalyst Pd (Pd/C) was used for comparison. The air breathing microfluidic fuel cell that used the PdAg/MWCNT electrocatalyst performed better (almost 70% more power) than the one that used the Pd/MWCNT electrocatalyst.

Various noble and non noble metal electrocatalysts like Zr/Ni alloy (Li et al., 2003a and 2003b), Ag or Ag/Pt (Amendola et al., 1999), Ni (Liu et al., 2003), $\text{ZrCr}_{0.8}\text{Ni}_{1.2}$ alloy (Lee et al., 2002), Pt and Au (Gyenge 2004) have been reported for the study of electrooxidation of sodium borohydride in traditional liquid alkaline fuel cell. Lee and Kim et al., (2012) investigated on a micro PEM fuel cell system with NaBH_4 generator. It was a catalytic microreactor comprised of hydrogen separator, micropump, and a NaBH_4 solution cartridge. However, very scanty literature is available for the electrooxidation of NaBH_4 in

air breathing microfluidic fuel cell. Elumalai et al., (2015) used unsupported Pt black nanoparticles as anode electrocatalyst. Brushett et al., (2009) investigated on microfluidic fuel cell using very high loading (10 mg/cm^2) of noble electrocatalyst Pt black at the anode.

2.1.2.1.2 Cathode Electrocatalysts

It is reported in the literature that the reaction kinetics of oxygen reduction is excellent in the alkaline medium compared to that in acidic medium. Selection of suitable cathode electrocatalyst is significant for an alkaline medium microfluidic fuel cell. At present Pt is most widely used cathode electrocatalyst in an alkaline microfluidic fuel cell. However, Pt is very expensive. For this reason, non noble metals e.g., MnO_2 (Yang et al., 2003), Co and Ni oxides (Rashkova et al., 2002), and Ag/C (Demarconnay et al., 2004) are used in place of platinum as electrocatalyst at cathode that makes the microfluidic fuel cell cheaper. The electrocatalysts for oxygen reduction in alkaline medium studied are Pt (Mitrovski et al., 2004, Cohen et al., 2005, Jayashree et al., 2006), Pd (Kjeang et al., 2007 Kjeang et al., 2008), Au (Kjeang et al., 2008), Silver oxide (Sung and Choi 2007), Bilirubin oxidase enzyme (Tago et al., 2008), Ag/Pt/CP (Abrego-Martinez et al., 2017). Gago et al., (2011) explored the potential of using carbon supported ruthenium chalcogenide (RuxSey/C) as a cathode electrocatalyst in a microfluidic fuel cell. The results were compared with those obtained using commercial Pt/C, and a better result was obtained using the Rux- Sey/C as the cathode electrocatalyst.

2.1.2.2 Fuel, Oxidant, and Electrolytes

2.1.2.2.1 Fuel for Anode

Mainly hydrogen or hydrogen rich molecules are preferred as fuel for feeding at the anode of a fuel cell. Thus, there are many fuels available including hydrogen (Mitrovski et al., 2006, Cohen 2005 and Mitrovski et al., 2004), methanol (Choban et al., 2005 and Jayashree et al., 2006), ethanol (Brushett et al., 2009), formic acid (Cohen et al., 2005 and Sun 2007), sodium borohydride (Brushett et al., 2009), hydrazine (Brushett et al., 2009), glucose (Cuevas-Muniz et al., 2011, Arjona et al., 2015 and Escalona-Villalpando et al., 2016), glycerol (Dector et al., 2013) and vanadium redox species (Ferrigno et al., 2002 and Kjeang et al., 2007).

Among liquid fuels, methanol and ethanol with energy densities of 6.09 kWh/Kg and 7.44 kWh/Kg have attracted more attentions for the use in microfluidic fuel cells. As already mentioned in introduction section that methanol is an attractive fuel because it is cheaper, easily available, no storage and handling problem, and soluble in aqueous electrolytes. Moreover, it releases 6 electrons per molecules of methanol. However, its low boiling point about 65 °C and toxicity are the major disadvantages. Methanol is not a primary fuel, and thus it is manufactured through complex chemical reaction, e.g., Fischer–Tropsch reaction.

In this context recent trend has seen in the search for such alcohol which is renewable and nontoxic. Ethanol is a good example of renewable fuel as it can be produced by fermentation of sugar containing biomass resources (Pramanik et al., 2007). It is nontoxic, high energy density and relatively high boiling point. It releases 12 electrons per molecules when electrochemically splitted at fuel cell anode. However, main drawbacks of ethanol are slow reaction kinetics in alkaline medium and breaking of C-C bond on pure Pt electrocatalyst.

Another hydrogen rich molecule NaBH_4 has been investigated as a potential source of hydrogen (Lee et al., 2012 and Schlesinger et al., 1953). It can be stored in the liquid phase and also it is the stable, nonflammable alkaline solution. NaBH_4 is also renewable and environmentally friendly fuel. In addition, the use of 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 (Schlesinger et al., 1953). Thus, methanol, ethanol, and NaBH_4 are considered as anode fuel for air breathing microfluidic fuel cell study in the thesis. Details of the reaction mechanism are discussed in the section 2.1.5.1 anode cyclic voltammetry study (page no. 36).

2.1.2.2.2 Oxidant for Cathode

There are several types of oxidants investigated in fuel cell cathode. They are available either in the gaseous or liquid or solid form like oxygen or air is the gaseous form, H_2O_2 in liquid form, and KMnO_4 and vanadium redox species and sodium hypochlorite is solid form. Irrespective of their state (solid/liquid/gas) they must be dissolved in the liquid electrolyte when they are in use in the fuel cell. Some oxidants as reported in literature are dissolved oxygen in aqueous form (Choban et al., 2005, Li et al., 2007, and Choban et al., 2004), air (Tominaka et al., 2008, Jayashree et al., 2005, Jayashree et al., 2006, Brushett et al., 2009 and Whipple et al., 2009), hydrogen peroxide (Kjeang et al., 2007 and Hasegawa et al., 2005), vanadium redox species (Ferrigno et al., 2002 and Kjeang et al., 2007), and sodium hypochlorite (Lee et al., 2003). It is well established that the oxygen reduction kinetics is excellent in the alkaline medium on Pt based electrocatalyst even at low temperatures (Ortiz et al., 2003). Thus, cathode activation loss is relatively low in

comparison to the anode. It is important to note that the diffusivity of gaseous oxidants (air/oxygen) in the liquid electrolyte is less in comparison to the liquid oxidant.

The exchange current densities (i_0) for oxygen reduction reaction on Pt electrocatalyst are six order of magnitude lower than that of hydrogen oxidation reaction at standard temperature (298 K) and pressure (1 atm). Due to this fact, oxidant dissolved oxygen has slow reaction kinetics in cathode compare to liquid oxidants when more power is drawn from the cell. It is needless to say that air breathing cathode improves the mass transport of oxygen from the bulk atmosphere to the cathode electrocatalyst sites by improving kinetics. An alternative of oxygen/air oxidant is highly soluble oxidant in aqueous solutions, e.g., KMnO_4 , H_2O_2 , etc. which reduces the mass transport limitation of dissolve oxygen in the electrolyte from bulk phase to the electrocatalyst sites. Choban et al., (2004) used oxygen saturated in 0.5 M sulfuric acid and 0.144 M potassium permanganate as oxidant at cathode separately. The anode fuel was 2.1 M formic acid. Potassium permanganate as oxidant produced higher current density due to the higher solubility of potassium permanganate in aqueous media. Li et al., (2007) used 0.1 M sulfuric acid solution saturated with oxygen as oxidant and 0.5 M formic acid in 0.1 M sulfuric acid solution as a fuel. The maximum power density of 0.58 mW/cm^2 was obtained due to insufficient supply of oxygen from the oxidant stream to the cathode. Some researchers (Tominaka et al., 2008, Jayashree et al., 2005, and Jayashree et al., 2006) have used air as an oxidant in air breathing microfluidic fuel cells. As the concentration of oxygen in the air is four orders of magnitude higher than in aqueous media (Jayashree et al., 2005). Thus, it generates higher power density when air breathing cathode is used in the microfluidic fuel cell.

2.1.2.2.3 Electrolytes

The microfluidic fuel cell uses liquid electrolytes either acidic or alkaline in nature, such as dilute sulfuric acid or potassium hydroxide solution which contains highly mobile H^+ or OH^- ions (Kjeang et al., 2008). In most microfluidic fuel cells, fuel and oxidant are dissolved in electrolytes and then fed into the micro channel using syringe pumps. An electrolyte transports ions and decreases the ohmic losses across the inter diffusion zone between the anode and cathode. Choban et al., (2004) showed that sulfuric acid (0.5 M) as supporting electrolyte, a maximum power density of 0.9 mW/cm^2 was obtained, on the other hand the maximum power density of 0.2 mW/cm^2 is obtained from the microfluidic fuel cell when only water is used. It proves that electrolyte improves the mobility of ions and thus reduces ohmic loss. Membraneless configuration allows the microfluidic fuel cell to operate either in alkaline or acidic medium, or under mixed medium condition. In the mixed medium condition, the cathode is in acidic medium and anode is in alkali medium, or vice versa (Choban et al., 2005). This flexibility enables to optimize the composition of anode and cathode streams individually, to maximize the individual electrode kinetics as well as the overall cell performance (Kjeang et al., 2007).

Choban et al., (2005) reported that the electrooxidation of alcohols in the alkaline medium could lead to electrocatalyst poisoning due to the formation of CO intermediates at the anode. However, the kinetics of oxygen reduction reaction is improved at the cathode. Brushett et al., (2009) investigated the performance of microfluidic fuel cell with ethanol and methanol as fuel under both acidic (sulfuric acid) and alkaline (potassium hydroxide) conditions, respectively. Methanol and ethanol showed improved performance in alkaline medium regarding power density, i.e., OCV of 1.2 V and power density of 17.2 mW/cm^2

for methanol and OCV of 0.7 V and power density of 12.1 mW/cm² for ethanol, respectively. Whereas, in acidic medium, OCV of 0.93 V and power density of 11.8 mW/cm² for methanol and OCV of 0.41 V and power density of 1.9 mW/cm² were obtained for ethanol. Improvement in the kinetics of alcohol electrooxidation and oxygen reduction in the alkaline medium resulting in the higher performance of the cell. Thus, in the present study all the experiments were performed using alkaline solution (KOH) as an electrolyte, and the effect of electrolyte (KOH) concentration have been discussed in the chapter 5 result and discussion (Page no. 107 to 110 and 117 to 123), for all fuels methanol, ethanol and sodium borohydride. Choban et al., (2005) performed the experiment using acidic (H₂SO₄), alkaline media (KOH) and mixed media (H₂SO₄/KOH) in a membraneless microfluidic fuel cell. Methanol (1 M) and dissolved oxygen were used as fuel and oxidant, respectively.

2.1.3 Electrode Fabrication and Characterization

Electrodes for air breathing microfluidic fuel cell should be porous in nature to ensure liquid fuel (methanol, or ethanol, or sodium borohydride) and oxidant (oxygen from the air) diffusion through the anode and cathode active zones, respectively. Moreover, the performance of microfluidic fuel cell depends on the successful development of anode and cathode. The anode and cathode fabrication and characterizations are discussed in this section.

2.1.3.1 Anode Fabrication

The fabrication technic of electrodes (anode/cathode) has an immense role on the overall performance of fuel cell. The electrodes (anode/cathode) are manufactured separately by a

wet fabrication method followed by drying and sintering of electrodes. At first, the anode electrocatalyst ink is prepared by dispersing the required quantity of electrocatalyst, a mixture of Nafion[®] ionomer and PTFE dispersion, which act as a binder. The electrocatalyst ink is pasted on a substrate called gas diffusion layer (GDL). The GDL/substrate is primarily carbon cloth or carbon paper (Shaegh et al., 2012, Thorson et al., 2012 Moore et al., 2011, Lam et al., 2012, and Shyu et al., 2015) or sometimes graphite plate (Choban et al., 2005, Sung et al., 2007, Priya et al., 2014, Jayashree et al., 2006) of 0.2 mm to 0.5 mm thickness and highly conducting for electrons. Before fixing electrocatalyst ink over GDL, it is hot pressed with supporting metallic material that is usually called the current collector. Graphite plate itself works as a current collector when graphite plate is used as a substrate for electrode fabrication. The current conductor should have excellent electron conducting properties to avoid ohmic loss. The electrocatalyst ink/slurry is then uniformly spread on the GDL in the form of a continuous wet film by rolling (Bever et al., 1998), painting (Ralph et al., 1997) or spray coating (Giorgi et al., 1998) techniques. Elumalai et al., (2015) fabricated electrode by graphite plates as current collectors and electrocatalyst substrate. For both electrodes, electrocatalyst suspensions were prepared by Pt black nanoparticles in a 10 wt. % Nafion[®] solution. This mixture is sonicated and hand painted at the faces of graphite plates. Then the solvent was evaporated by heating. Pramanik et al., (2017) fabricated electrode by simple paint brush technique using Toray carbon paper as GDL and Ni mesh as the current collector.

2.1.3.2 Cathode Fabrication

Microfluidic cell performance depends on the oxidant's concentration at the electrocatalyst sites and diffusivity through the electrolyte solution. Air breathing cathode structure allows

gaseous oxygen transport from the ambient air to the electrocatalyst sites and does not allow liquid crossover through the cathode. Moreover, three phase contact, i.e., solid (electrocatalyst), liquid (electrolyte), and gas (oxidant oxygen) is very important for air breathing cathode during microfluidic fluidic fuel cell operation (Fig 2.1).

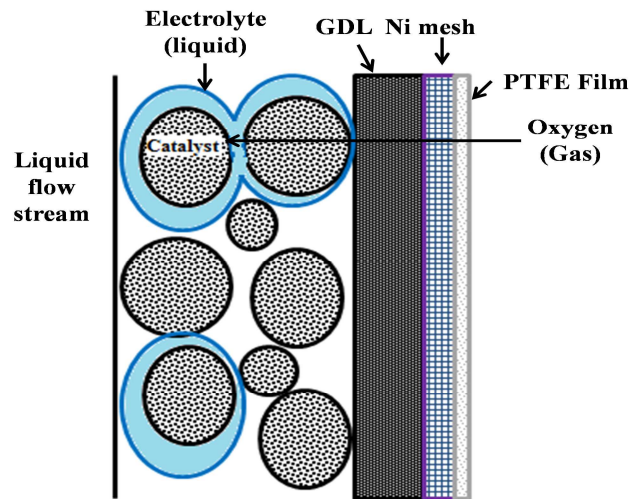


Figure 2.1 Three phase contact at air breathing cathode.

2.1.3.2.1 Air Breathing Cathode

The literature on the fabrication of air breathing cathode is very scanty. Generally, the cathode electrocatalyst ink is prepared using a similar method as for the anode. First of all the three layers of air breathing cathode composite is made keeping the current collector (Ni mesh) between the gas diffusion layer (GDL) and air breathing PTFE film (Pramanik et al., 2017). The gas diffusion layer, current collector and extreme outer layer of current collector PTFE film are attached by hot press using similar conditions. The electrocatalyst is pasted on GDL side using paint brush followed by drying and sintering (Rathoure et al., 2016). Jayashree et al., (2005) introduced the first microfluidic fuel cell with the integrated air breathing cathode. Many investigators (Jayashree et al., 2006, Brushett et al., 2009,

Hollinger et al., 2010, Whipple et al., 2009, Shaegh et al., 2012, Thorson et al., 2012, Lopez-Rico et al., 2015, Armenta-Gonzalez et al., (2016), and Abrego-Martinez et al., 2017,) worked in microfluidic fuel cell with air breathing cathode in alkaline medium.

2.1.4 Electrode Characterizations

The characterizations of manufactured electrodes are very important before they are used or recommend for microfluidic fuel cell application. Physical and electrochemical techniques are used for the study of electrodes. Electrodes are characterized to know the activity of the electrodes. Most of the literature described the electrocatalysts properties regarding their surface area per unit mass of the electrode, SEM or TEM for surface morphology, porosity and lattice structure. Further, half-cell analysis is constructed with a reference electrode, working electrode and counter electrode to study the reaction mechanism through cyclic voltammetry. The working electrode is electrochemically analyzed to predict the formation of intermediate products, poisoning species. Moreover, the reaction mechanism is established with the help of cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometry, etc. Table (2.1) to (2.4) shows the electrode fabrication methods by various investigators and the outcome of their analyses for methanol, ethanol, and sodium borohydride electrooxidation at anode and oxygen reduction at the cathode in alkaline medium. In the following section, 2.1.5 half-cell analyses of anode and cathode are discussed in detail.

2.1.5 Half-cell Analyses

Half-cell analysis is performed to identify the performance limiting factors of the microfluidic fuel cell using three electrode cell assembly. It also provides the information

about electrocatalyst activity of electrodes for electrooxidation and reduction reaction. The reference electrode is used to measure the voltage losses due to different limiting parameters of an electrochemical system such as kinetics, mass transfer and ohmic resistances of individual electrodes.

Table 2.1 Electrocatalyst fabrication for methanol electrooxidation at anode in alkaline condition and techniques used for analysis of the system

Subject of investigation/Major technique	System information for methanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics and mechanism of methanol oxidation/ Cyclic voltammetry	Pt-Ru nanoparticles	H ₂ SO ₄ KOH	Electrocatalyst (Pt-Ru & Pt) suspension was prepared than applied to those side faces of the graphite plate electrodes that line the microfluidic channel.	Shows the comparison of a microfluidic fuel cell in acidic and alkaline media. MFC operating under alkaline condition has +ve effects on the reaction kinetics at both anode and cathode.	Choban et al., (2005)

Subject of investigation/Major technique	System information for methanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics of methanol oxidation / Cyclic voltammetry / Chronoamperometry	Pt-Ru	H ₂ SO ₄ KOH	Catalyst ink of Pt-Ru was added onto the exposed area of the graphite plate anode. Toray carbon paper with a Pt electrocatalyst was used as the cathode.	Shows that the performance of MFC operating in alkaline medium is better than operating in the acidic medium under identical reaction conditions.	Jayshree et al., (2006)
Reaction kinetics and mechanism of methanol / Cyclic voltammetry	Nickel hydroxide	KOH	Anode and cathode were prepared by electro deposition of nickel hydroxide and silver oxide, respectively.	Developed a novel liquid based micro scale fuel cell using nonnoble electrocatalysts.	Sung and Choi (2007)

Subject of investigation/Major technique	System information for methanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Electrooxidation of methanol / Chronoamperometry / Scanning electron microscope / XRD / XPS	Pt/CP	KOH	Ag/Pt/CP as cathode electrocatalyst and Pt/CP as anode electrocatalyst were synthesized and deposited on CP substrate by PLD using 20,000 laser pulses for each metal.	Methanol tolerant Ag/Pt/CP cathode electrocatalyst was synthesized to reduce the methanol crossover in membraneless microfluidic fuel cell working in the alkaline medium.	Abrego-Martinez et al., (2017)
Methanol electrooxidation / stacking efficiency analysis	Pt-Ru black	KOH	Electrodes were fabricated by spraying the electrocatalyst ink (Pt-Ru and Pt/C) on the carbon paper	A six cell vapor feed microfluidic fuel cell stack (in series) was proposed to deal with the fluidic management.	Wang et al., (2016)

Subject of investigation/Major technique	System information for methanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Methanol electrooxidation / Cyclic voltammetry / electrochemical impedance spectroscopy	Pt-Ru black	KOH	Catalyst ink (Pt-Ru black at the anode and Pt black at the cathode) was painted on graphite plate as an anode and Toray carbon paper as the cathode, respectively.	Investigated the performance of airbreathing microfluidic fuel cell in the acidic or alkaline medium.	Brushett et al., (2009)

Table 2.2 Electrocatalyst fabrication for ethanol electrooxidation at anode in alkaline condition and techniques used for analysis of the system

Subject of investigation/Major technique	System information for ethanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Ethanol electrooxidation / Cyclic voltammetry / electrochemical impedance spectroscopy	Pt-Ru black	KOH	Catalyst ink (Pt-Ru black at the anode and Pt black at the cathode) was painted on graphite plate as an anode and Toray carbon paper as the cathode, respectively.	Investigated the performance of air breathing microfluidic fuel cell in the acidic or alkaline medium.	Brushett et al., (2009)

Subject of investigation/Major technique	System information for ethanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics and mechanism of ethanol	Pt black	KOH	Unsupported platinum black nanoparticles (Alpha Aesar) are applied to the sides of the graphite plates (kiriti graphite), which act as anode and cathode.	Investigated the electrocatalytic oxidation of ethanol on membraneless sodium percarbonate fuel cell using platinum electrodes in the alkaline, acidic medium.	Priya et al., (2014)
Ethanol electrooxidation / X-ray diffraction / TEM micrographs	Commercial Pd/C Synthesized Pd/C	KOH	Electrocatalyst (Pd/C) was deposited on carbon nanofoam by spray coating technique as anode and cathode.	Investigated the role of pH in the cell performance using Pd based electrocatalysts.	Lopez-Rico et al., (2015)

Subject of investigation/Major technique	System information for ethanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics and mechanism of ethanol / X-ray diffraction / TEM micrographs / Cyclic voltammetry / TGA	Pd-NiO/C	KOH	Synthesized Pd-NiO/C and commercial Pt/C electrocatalysts were deposited on carbon nanofoam slides using spray ink method as anode and cathode, respectively.	Synthesized the Pd-NiO/C electrocatalyst and compare the performance of membraneless co-laminar fuel cell in the different medium.	Lopez-Rico et al., (2016)

Subject of investigation/Major technique	System information for ethanol electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics and mechanism of ethanol / X-ray diffraction / TEM micrographs / Cyclic voltammetry / Thermogravimetric analysis / X-ray fluorescence	Pd/MWCNT PdAg/MWCNT	KOH	Electrocatalysts (Pd/MWCNT and PdAg/MWCNT) were applied on the surface of Toray carbon paper as the anode and cathode.	Synthesized two electrocatalysts based on Pd using for ethanol electrooxidation in air breathing microfluidic fuel cell to compare the performance with commercial Pd/C electrocatalyst.	Armenta-Gonzalez et al., (2016)

Table 2.3 Electrocatalyst fabrication for sodium borohydride electrooxidation at anode in alkaline condition and techniques used for analysis of the system

Subject of investigation/Major technique	System information for NaBH ₄ electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode	Electrolyte			
Sodium borohydride electrooxidation / Cyclic voltammetry / electrochemical impedance spectroscopy	Pt black	KOH H ₂ SO ₄	Electrocatalyst ink (Pt black) was painted on graphite plate as an anode and Toray carbon paper as the cathode, respectively.	Investigated the performance of air breathing microfluidic fuel cell in the acidic or alkaline medium. MFC gives better performance in alkaline medium.	Brushett et al., (2009)

Subject of investigation/Major technique	System information for NaBH ₄ electrooxidation		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Reaction kinetics and mechanism of Sodium borohydride	Pt black nanoparticle	NaOH	Unsupported platinum black nanoparticles are applied to the sides of the graphite plates as anode and cathode.	Fabricated a MFC using sodium borohydride as fuel and sodium perborate as oxidant and compare the performance in alkaline and acidic medium.	Elumalai et al., (2015)

Table 2.4 Electrocatalyst fabrication for oxygen reduction at cathode in alkaline condition and techniques used for analysis of the system

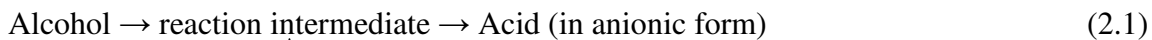
Subject of investigation/Major technique	System information for oxygen reduction		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Oxygen electroreduction / Cyclic voltammetry / RRDE / RDE / SEM / XPS / EIS	Pt/C Cu/C Pt-Cu/C	KOH	Electrodes (Pt/C, Pt-Cu/C, and Cu/C) were fabricated by polishing with alumina suspension and immersing them into the solution of CuSO ₄ and H ₂ PtCl ₆ .	Synthesized Pt-Cu/C has excellent electrocatalytic activity, and the ORR compare to Pt/C and Cu/C and is a four electron reduction pathway.	Lu et al., (2015)

Subject of investigation/Major technique	System information for oxygen reduction		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electrocatalyst	Electrolyte			
Oxygen electroreduction / Cyclic voltammetry / RDE / SEM / XPS	Pt/C Pt-NB/G Pt-NB/C	KOH	Electrocatalyst (Pt-NB/G and Pt-NB/C) were synthesized using ethylene glycol method. Electrodes were fabricated by polishing the electrocatalyst ink on glassy carbon paper.	Investigated that the NB modified graphene nanosheets can be good Pt electrocatalyst support with high stability and excellent electrocatalytic properties.	Hussain et al., (2017)
Electrochemical reduction of oxygen / RRDE	Ag/C Pt/C	NaOH	Electrocatalyst synthesized by colloidal precursor method. An electrode prepared by painting catalyzed ink on the glossy carbon substrate.	The mechanism of oxygen electroreduction on Ag/C is similar to Pt/C electrocatalyst.	Demarconnay et al., (2004)

Subject of investigation/Major technique	System information for oxygen reduction		Electrocatalyst and electrode preparation technique	Remarks	References
	Anode Electro-catalyst	Electrolyte			
Oxygen electro-reduction / Cyclic voltammetry / XRD	Nanoporous amorphous manganese oxide	KOH	Electrocatalyst was synthesized by sol gel method. Electrodes were prepared by painting electrocatalyst ink on carbon paper.	Higher corrosion resistance is found in crystalline MnO ₂ than amorphous MnO ₂ .	Yang et al., (2003)

2.1.5.1 Anode Cyclic Voltammetry

The comparison of various techniques used for methanol, ethanol, and sodium borohydride electrooxidation at the anode and their analysis are given in table (2.1), (2.2) and (2.3), respectively. The most commonly used technique in electrochemical studies of fuel cell reaction has been cyclic voltammetry. The cyclic voltammetry (CV) is used to study the redox behavior of electrodes in the fuel electrolyte mixture (Bard and Faulkner 2001). The cyclic voltammogram helps in predicting reaction mechanism, intermediates and electrolyte/fuel mixtures, such that the redox reaction occurs at lowest potential and the formation of poisoning species can be prevented. The existence of the reactive intermediate and the inactive intermediates (poisoning species) generated during alcohol (methanol, ethanol...etc) electrooxidation in an alkaline solution suggests a dual path reaction mechanism (Equation 2.1 and 2.2), which is summarized as below (Tripkovic et al., 2001 and Verma A., 2005).

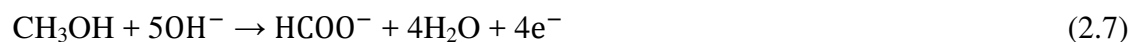


The path is shown by equation (2.1) is the main reaction path which could also be suggested for the oxidation of other alcohols used. It is assumed the formation of reactive intermediates, produced by alcohol dehydrogenation (Equation 2.3), and OH_{ad} species formed by the OH^- anion adsorption (Equation 2.4) and the corresponding acids (Equation 2.5) as reaction products existing in the form of anions (Equation 2.6) in alkaline solutions.





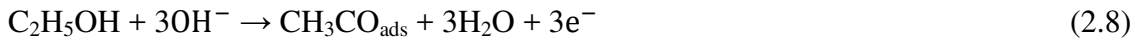
The overall electrooxidation reaction (Equation 2.7) of methanol resulting in four electrons and one water molecule. It is also seen in the equation (2.7) that the methanol electrooxidation reaction follows the following reaction giving formate ions (Pandey et al., 2009).



However, it was first observed by electrochemically modulated infrared reactance spectroscopy (EMIRS) that CO is the main poisoning species formed during the chemisorption and oxidation of methanol on the platinum electrode (Beden et al., 1981). Formaldehyde (HCHO), and formic acid (HCOOH) and final product CO₂ were also analyzed as intermediate reaction products by liquid or gas chromatography (Belgsir et al., 1987).

Lu et al., (2015) investigate the electrooxidation of methanol on AuNi/C electrocatalyst in alkaline medium. The alloying by heat and acid treatment was performed between Au and Ni, and the removal of unalloyed Ni is achieved. Their electrochemical results show that the alloying treatment process is favorable to improve the electrocatalytic activity of the AuNi/C electrocatalyst.

The general mechanism for the electro oxidation of ethanol in alkaline medium, which involves the electrooxidation of ethanol to acetate ions at the anode, can be summarized as follows (Pandey et al., 2009).



The electrocatalytic oxidation of ethanol has been studied on different platinum based electrocatalysts, including Pt-X alloys (X = Ru, Sn, Mo ...). Acetaldehyde (CH_3COOH) and acetic acid (CH_3CHO) were identified in the final product by infrared spectroscopy (Hitmi et al., 1994 and Iwasita et al., 1994). The complete electrooxidation reactions of alcohols produce CO_2 as a final product. Since alcohol group contains one oxygen atom, the extra oxygen atom must be provided by water or water adsorbed residues generated on the cathode side by oxygen reduction for the formation of CO_2 as the final product (Lamy et al., 2001). Spendelov et al., (2004) proposed a mechanism in the alkaline medium for electrooxidation of adsorbed CO on Pt (111) and Pt (111)/Ru. The mechanism involves the attack by solution phase OH^- on the adsorbed CO (Equation 2.12):



They reported that the CO stripping on Pt (111)/Ru electrocatalyst occurs at the lower potential than that of pure Pt (111). This implies the advantage for electrooxidation of methanol and, most probably, other small organic molecules that produce CO as an intermediate and/or poisoning species during electrooxidation.

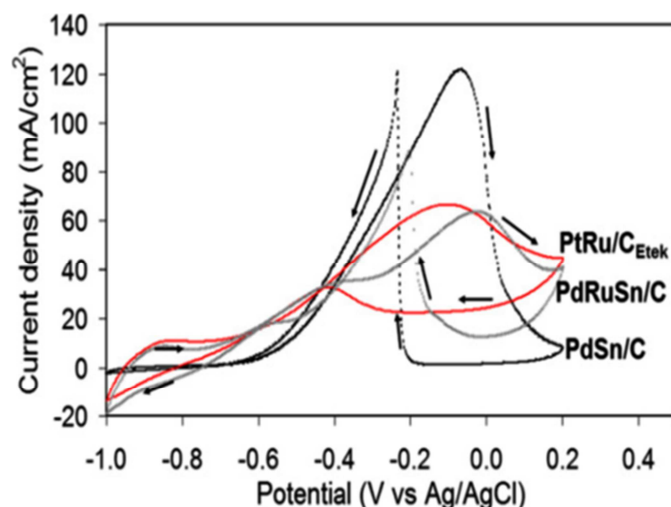


Figure 2.2 Cyclic voltammograms of Pd-Sn/C, Pd-Ru-Sn/C and 40 wt % Pt-Ru/C (E-TEK Inc.) nanocatalysts in 0.5 M NaOH + 3 M ethanol at room temperature. Scan rate 50 mV/s 3rd cycle was used in this analysis.

Modibedi et al., (2011) compared the electrooxidation ethanol on of Pd-Sn/C and Pd-Ru-Sn/C electrocatalysts to that of Pt-Ru/C (E-TEK Inc.) in 3 M ethanol mixed with 0.5 M NaOH (Fig 2.2). The cyclic voltammograms show that Pd-Sn/C, Pd-Ru-Sn/C and Pt-Ru/C (E-TEK Inc.) nano electrocatalysts are active towards ethanol electrooxidation in alkaline medium. However, electrocatalyst Pd-Sn/C and Pt-Ru/C (E-TEK Inc.) show the maximum current densities of 121.59 mA/cm² at -0.062 V and 66.39 mA/cm² at -0.10 V, respectively. The current density decreases with the increase in potential above -0.062 V and -0.10 V for Pd-Sn/C and Pt-Ru/C (E-TEK Inc.) respectively, due to the formation of oxides on the electrocatalyst surface and hence blocking the further oxidation of ethanol. At this stage,

the electrocatalytic activity decreases and can be recovered during the reverse scan, as shown by the peak at about -0.23 V and -0.40 V for Pd-Sn/C and Pt-Ru/C (E-TEK Inc.), respectively. This peak can be due to the oxidative decomposition of byproducts. The cyclic voltammogram for electrocatalyst Pd-Ru-Sn/C shows a broad peak in the forward scan, with two maxima, and a single oxidation peak in the reverse scan. The electrocatalyst shows a more negative potential of -0.746 V than Pd-Sn/C (-0.670) and Pt-Ru/C (E-TEK Inc.) (-0.679). This implies an improvement in the kinetics of ethanol electrooxidation on Pd-Ru-Sn/C than on Pd-Sn/C electrocatalyst.

Sodium borohydride (NaBH_4) shows two types of possible routes for the electrooxidation as reported in the literature. In the first type, NaBH_4 is directly oxidized as per the equation (2.13) below (Li et al., 2003a, Li et al., 2003b, Amendola et al., 1999 and Pramanik et al., 2017):



And in the second type, hydrogen gas is liberated at high temperature or pH less than 7 and this hydrogen gas reacts with OH^- to produce electrons (Equation 2.14 to 2.15).



Because of the hydrolysis reaction, 7 electrons are utilized per molecule of borohydride electrooxidation instead of theoretically 8 electrons (Wang et al., 2014).

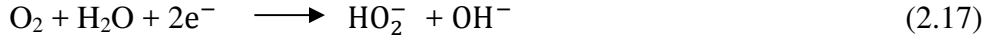
2.1.5.2 Cathode Cyclic Voltammetry

The oxygen reduction reaction (ORR) in alkaline solution proceeds mainly by two pathways (i) single step 4 electron reduction pathway and (ii) two step 2+2 electron reduction pathway (Ortiz et al., 2003). In low temperature fuel cells, the oxygen reduction reaction occurring at the cathode usually is very slow in the absence of electrocatalyst. To speed up the ORR kinetics up to a desired usable level in the fuel cell, a cathode ORR electrocatalyst is required. Presently, Pt or Pt based materials are the most widely used electrocatalysts. However, Pt or Pt based electrocatalysts are very expensive for the practical use in the microfluidic fuel cell. Thus, a lot of research over the past few decades has focused on developing alternative of Pt including nonnoble metal electrocatalysts (Zhang et al., 2006). The electrocatalytic role for the ORR mechanism and its kinetic parameters, such as Tafel slopes and exchange current densities, can be obtained from techniques such as cyclic voltammetry, steady state polarization, rotating ring disk electrode, and rotating disk electrode (Song et al., 2008). Oxygen reduction reaction on other metal surfaces such as Au, Ir, Rh, etc. has also been investigated (Hoare 1968). However, these metals show lower electrocatalytic activity towards ORR than Pt.

The direct oxygen reduction to OH^- ions, i.e., single step 4 electron pathway (Equation 2.16) is described below (Ortiz et al., 2003 and Rathoure et al., 2016):



Or an oxygen reduction to HO_2^- ions i.e., two electron pathway:



With subsequent reduction of peroxide ions to OH^- ions, i.e., two electron pathway



Equations (2.17) and (2.18) are collectively produce 2+2 electron mechanism.

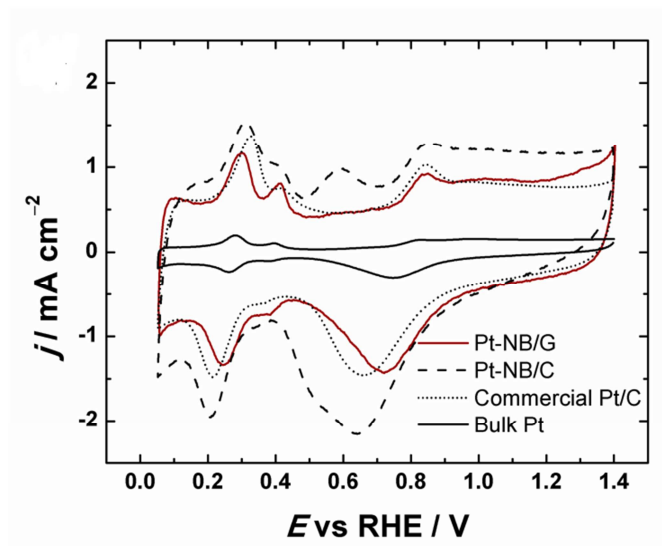


Figure 2.3 Cyclic voltammograms of Pt-NB/G, Pt-NB/C, commercial Pt/C modified GC and bulk Pt electrodes in Air-saturated 0.1 M KOH solution; Scan rate: 50 mV/s.

Hussain et al., (2017) performed experiments to study the electrocatalytic properties of Pt nanoparticles supported on nitrobenzene modified grapheme (Pt-NB/G) as a electrocatalyst for oxygen reduction reaction in alkaline medium. Graphene nanosheets were spontaneously grafted with nitrophenyl groups using 4 nitrobenzenediazonium salts. The electrocatalytic activity and stability of prepared electrocatalyst towards the oxygen reduction reaction in 0.1 M KOH solution have been studied and compared with that of the

commercial Pt/C electrocatalyst. The result shows that the NB (Nitrobenzene) modified graphene nano sheets can be good Pt electrocatalyst support with high stability and excellent electrocatalytic properties. The current density on Pt-NB/G for O₂ reduction was 0.184 mA/cm² which, is very close to that obtained for commercial 20 wt. % Pt/C electrocatalyst, i.e., 0.214 mA/cm² at 0.9 V. The Pt-NB/G electrocatalyst support a four electron single step reduction mechanism of oxygen and can be used as a promising cathode electrocatalyst in alkaline microfluidic fuel cells. Lu et al., (2015) synthesized Pt-Cu support carbon for oxygen reduction and performed cyclic voltammetry test for ORR at ambient temperature. The catalytic activity of Pt-Cu/C, Pt/C, and Cu/C were compared using CV, rotating disk electrode, rotating ring disk and electrochemical impedance spectroscopy to obtain the kinetics and the reaction mechanisms of the ORR. The results show that the synthesized Pt-Cu/C has excellent electrocatalytic activity and supports the four electrons reduction pathway for oxygen reduction reaction. Genies et al., (1998) studied the effect of electrocatalyst particle size on the catalytic activity for oxygen reduction reaction in alkaline medium. A little loss in catalytic activity was observed with the decrease in particle size for ORR in alkaline medium. The activity loss of electrocatalyst might be because of the stronger adsorption of oxygen generated species. The ORR on Pt particles supports four electron mechanism. From the literature, it is clear that Pt based electrocatalyst is highly effective for ORR in alkaline medium. Thus, in this thesis, Pt based commercial electrocatalyst was used for cathode fabrication.

2.1.6 Cell Performance

Published literature on microfluidic fuel cell suggests that, it is emerging as a breakthrough technology towards the production of low cost electricity for portable electronics devices

and biomedical healthcare diagnostics appliances. Many investigators have started working on electrooxidation of methanol, ethanol, or sodium borohydride and reduction of oxygen in alkaline medium in a half-cell analysis as discussed in the previous section (Verma et al., 2005b). However, very scanty literature is available on the microfluidic fuel cell using methanol, or ethanol, or sodium borohydride as fuel in alkaline medium. Almost no literature is available on air breathing microfluidic fuel cell study in detail using methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and sodium borohydride (NaBH_4). Jayshree et al., (2006) worked on methanol/air microfluidic fuel cell with air breathing cathode. The anode and cathode electrocatalyst were the very high loading of Pt-Ru (50:50) of 10 mg/cm^2 and Pt of 2 mg/cm^2 , respectively. The maximum OCV of 1.05 V, current density of 120 mA/cm^2 and power density of 17 mW/cm^2 was obtained, respectively.

Only a few studies on ethanol fuel in the microfluidic fuel cell using bio anode have been reported (Moore et al., 2005). Pramanik et al., (2015) performed experiments on ethanol/air microfluidic fuel cell with air breathing cathode. The anode and cathode electrocatalyst were at low loading of Pt-Ru (30 %:15 % by wt.)/ C_{HSA} of 1 mg/cm^2 and Pt (40 % by wt.)/ C_{HSA} of 1 mg/cm^2 , respectively. The maximum OCV of 0.43 V, current density of 31.33 mA/cm^2 and power density of 2.97 mW/cm^2 were obtained, respectively. Similarly, limited researches have been reported using NaBH_4 as fuel and liquid H_2O_2 as oxidant with traditional PEM based design (Kjeang et al., 2009). The NaBH_4 solution has also been tested in the alkaline fuel cell (AFC) using KOH solution as an electrolyte in spite of their many disadvantages (Verma et al., 2005d). However, NaBH_4 as fuel in air breathing microfluidic fuel cell have never been investigated earlier. Elumalai et al., (2015) studied on the membraneless sodium perborate fuel cell.

Table 2.5 Performance of microfluidic fuel cell using methanol, ethanol and sodium borohydride as fuel in alkaline medium

References	Electrocatalysts	Other operating parameters	Power density (mW/cm ²)	OCV (V)
Choban et al., (2005)	Anode: Pt-Ru nanoparticles loading: 2 mg/cm ² Cathode: Pt black nanoparticles loading: 2 mg/cm ²	Fuel: Methanol Oxidant: Oxygen (aq., sat.) Y-shape Temperature: room temperature	12	1.4
Jayshree et al., (2006)	Anode: Pt-Ru loading: 10 mg/cm ² Cathode: Pt loading: 2 mg/cm ²	Fuel: Methanol Oxidant: Air F-shape Air breathing Temperature: room temperature	17	1.05
Sung and Choi (2007)	Anode: Nickel hydroxide loading: Not available Cathode: Silver oxide loading: Not available	Fuel: Methanol Oxidant: H ₂ O ₂ I-shape Temperature: 22.5 °C	0.03	0.11

References	Electrocatalysts	Other operating parameters	Power density (mW/cm ²)	OCV (V)
Abrego-Martinez et al., (2017)	Anode: Pt/CP loading: Not available Cathode: Ag/Pt/CP loading: Not available	Fuel: Methanol Oxidant: Air V-shape Air breathing Temperature: Ambient	2.4	0.55
Wang et al., (2016)	Anode: Pt-Ru black loading: 10 mg/cm ² Cathode: Pt/C loading: 1.2 mg/cm ²	Fuel: Methanol vapor Oxidant: Air Air breathing Six cell stack Temperature: 60 °C	108.7	5 - 5.5
Brushett et al., (2009)	Anode: Pt-Ru black Pt-Ru black Pt loading: 10 mg/cm ² Cathode: Pt black loading: 2 mg/cm ²	Anode: CH ₃ OH C ₂ H ₅ OH NaBH ₄ Cathode: Air Air breathing	17.2 12.1 101	Not Available

References	Electrocatalysts	Other operating parameters	Power density (mW/cm ²)	OCV (V)
Priya et al., (2014)	Anode: Pt black loading: 2 mg/cm ² Cathode: Pt black loading: 2 mg/cm ²	Anode: C ₂ H ₅ OH Cathode: Sodium percarbonate E-shape Temperature: room temperature	2.53	0.95
Elumalai et al., (2015)	Anode: Pt black nanoparticle loading: 2 mg/cm ² Cathode: Pt black nanoparticle loading: 2 mg/cm ²	Anode: NaBH ₄ Cathode: perborate + H ₂ SO ₄ E-shape Temperature: room temperature	27.75	Not Available
Lopez-Rico et al., (2015)	Anode: Commercial Pd/C Synthesized Pd/C loading: 6 mg/cm ² Cathode: Commercial Pd/C loading: 6 mg/cm ²	Anode: Ethanol Cathode: Oxygen/Air	15.94 15.37	Not Available

References	Electrocatalysts	Other operating parameters	Power density (mW/cm ²)	OCV (V)
Lopez-Rico et al., (2016)	Anode: Pd-NiO/C loading: 66.67 mg/cm ² Cathode: Pt/C loading: 66.67 mg/cm ²	Anode: Ethanol Cathode: H ₂ O ₂ Air breathing Temperature: room temperature	108 85.5	1.11 1.05
Armenta-Gonzalez et al., (2016)	Anode: Pd/MWCNT Pd-Ag/MWCNT loading: 22.22 mg/cm ² Cathode: Pt/C loading: 22.22 mg/cm ²	Anode: Ethanol Cathode: Air Y-shape Air breathing Temperature: room temperature	4.4 14.5	0.64 0.95

They used alkaline solution of NaBH₄ as fuel and Acidic perborate as an oxidant. The maximum power density of 27.75 mW/cm² was obtained with 0.15 M NaBH₄ as fuel in 3 M NaOH solution as an electrolyte. Table (2.5) shows the salient features of the different studies on microfluidic fuel cell by several investigators. Microfluidic fuel cell with air breathing cathode has several advantages like, (i) air breathing cathode can be combined with another oxidant which is highly soluble in the electrolyte (Pramanik et al., 2017). (ii)

Oxygen from the air is directly introduced at cathode. Thus, no oxygen storage is required and (iii) oxygen is available in plenty amount (21%) in the atmosphere that has no cost.

It is evident from the literature that air breathing microfluidic fuel cell performance depends on the successful manufacturing of anode, air breathing cathode, microfluidic fuel cell design and machining, current collector design, sealing material, stack development, and its auxiliaries. Moreover, microfluidic fuel cells have certain challenges due to its smaller size (micro dimension). Both, micro channel and electrode geometry play an important role in mass transport and inter diffusive zone. Ahmad et al., (2008) reported that by optimizing the channel dimensions and reaction surface areas, fuel utilization could be improved by up to 86%. Sun et al., (2007) showed that optimized flow rate could enhance the open circuit potential which is an indication for controlling the diffusive crossover of fuel. Hollinger et al., (2010) attached a thin porous layer of polycarbonate at the fuel electrolyte interface which reduced the liquid-liquid contact between the two streams by 98.8% resulting in the reduction of the fuel crossover.

Gas bubble generation within the channel in the microfluidic fuel cell is another performance limiting factor. It may disturb the interface leading to uncontrolled mixing of streams and performance degradation. The gas bubbles generated in the channel can reduce the performance of the cell by (i) decreasing the effective electrode area and (ii) the destruction of the liquid-liquid interface. Generation of gas bubble in the channel can be minimized by controlling the flow rate of the two streams which results to reduce diffusive mixing and fuel crossover, or utilizing a grooved micro channel geometry (Kjeang et al., 2007), or using porous separator at the liquid-liquid interface (Hollinger et al., 2010), or optimizing the channel geometry and tailoring the electrode geometry (Ebrahimi et al.,

2010, Ahmed et al., 2008, Bazylak et al., 2005). When microfluidic fuel cell using H_2O_2 as an oxidant, oxygen generation occurs in the channel due to the spontaneous decomposition of H_2O_2 (Hasegawa et al., 2005). Similarly, microfluidic fuel cell running on formic acid as a fuel and H_2O_2 as an oxidant can generate bubbles (Kjeang et al., 2007). Moreover, carbon dioxide can be produced from the oxidation of formic acid, methanol and ethanol, etc. (Shyu et al., 2010). Li et al., (2007) performed experiments using H_2O_2 as oxidant resulted in the fluctuation of open circuit potential because of generation of oxygen bubbles.

It is clear from the above discussion that there is a need of detail study on air breathing microfluidic fuel cell based in alkaline medium to determine optimum conditions, e.g., fuel concentration, electrocatalyst loading at anode and cathode, electrocatalyst type, electrolyte concentration and temperature, etc. such that maximum cell performance in terms of power density and current density is obtained. Usually, electrocatalyst loading in the microfluidic fuel cell is quite high as reported in the literature. Here, a special emphasis was given to keep the electrocatalyst loading as low as possible, i.e., in the range of 0.5 mg/cm^2 to 2 mg/cm^2 . Moreover, special care was taken for manufacturing of good quality air diffusion/breathing cathode and a porous anode which helps to obtain better output from the air breathing microfluidic fuel cell.

2.2 Objectives

The detailed literature review reveals that development work on air breathing microfluidic fuel cell in alkaline media based on methanol, ethanol, and sodium borohydride fuel is required as half-cell analysis and single study show promising results in term of current density and cell voltage. A detailed study is required to completely understand the various phenomena take place in anode, cathode, and electrolyte of the microfluidic fuel cell. Towards the fulfilling of these requirements, the thesis has following objectives.

1. To fabricate anode and cathode with noble metal electrocatalysts.
2. To study the electrode morphology with scanning electron microscope (SEM) and analysis of anode and cathode through half-cell using cyclic voltammetry (CV) in three electrode cell assembly to understand reaction kinetics and mechanism.
3. To study the reaction kinetics of fuel (methanol, ethanol and sodium borohydride) oxidation and oxygen reduction based on cyclic voltammetry results.
4. To perform experiments on air breathing microfluidic fuel cell to determine optimum condition of different parameters, e.g., the concentration of fuel, temperature, electrocatalysts loading, the different type of electrocatalysts at anode and cathode, oxidant at the cathode (air/oxygen), such that maximum power density is obtained. The gas diffusion layer (GDL) is also synthesized in the laboratory to compare its performance with the commercial GDL/Toray carbon paper procured from Alfa Aesar, USA.

5. To study stability test of air breathing microfluidic fuel cell.
6. Mathematical modeling of air breathing microfluidic fuel cell and comparison of the same with the experimental data.

The next chapter describes the experimental detail related to the development of air breathing microfluidic fuel cell in alkaline media, e.g., anode and cathode preparation and properties, half-cell analysis through cyclic voltammetry, single cell performance and stability test of the single cell.