

## CHAPTER 3

### EXPERIMENTAL

#### 3.1 Material

The electrocatalysts used to prepare the anodes were Pt-Ru (30 %:15 % by wt.)/High Surface Area Carbon ( $C_{HSA}$ ) (Alfa Aesar, USA) and Pt (40 % by wt.)/ $C_{HSA}$  (Alfa Aesar, USA). The cathodes were prepared by Pt (40 % by wt.)/ $C_{HSA}$  (Alfa Aesar, USA). The following table (3.1) shows the properties of Pt-Ru/ $C_{HSA}$  and Pt/ $C_{HSA}$  electrocatalysts.

**Table 3.1 Properties of Electrocatalysts**

Electrocatalysts (Alfa Aesar, USA)	Specific Surface Area* ( $m^2 gm^{-1}$ )
Pt-Ru (30 %:15 % by wt.)/ $C_{HSA}$	103.06
Pt (40 % by wt.)/ $C_{HSA}$	352.81

Toray Carbon paper (TGP-H-60 Alfa Aesar, USA) was used as substrate or gas diffusion layer (GDL) for the catalyst ink. In some microfluidic fuel cell experiments, IIT (BHU) laboratory made carbon cloth was also used as GDL. The typical composition and properties of the Toray Carbon paper (TGP-H-60 Alfa Aesar, USA) is given in table (3.2). Nafion<sup>®</sup> (D-520) and Poly tetra fluoro ethylene (PTFE) (10 wt. %) dispersion were

---

\* Surface area was measured by surface area analyzer: smart sorb 92/93 in IIT (BHU) laboratory.

obtained from Alfa Aesar, USA, and Sigma Aldrich, USA, respectively. The mixture of Nafion<sup>®</sup> and PTFE were used as a binder. The composition of Nafion<sup>®</sup> dispersion and PTFE dispersion are given in table (3.3) and (3.4), respectively. Pure nickel mesh was used as a current collector because it is highly resistive to alkali and good electrical conductor. Microfluidic fuel cell setup was made of Perspex sheet. Methanol, ethanol, and NaBH<sub>4</sub> of analytical grade were used as anode fuel. Methanol and ethanol were obtained from Fisher Scientific, India. Sodium borohydride was obtained from Loba Chemie. Pvt. Ltd., Mumbai. Atmospheric oxygen (air) and H<sub>2</sub>O<sub>2</sub> (Fisher Scientific, India) were used as an oxidant. Isopropanol (Fisher Scientific, India) was used as diluent. PTFE film was used for air breathing cathode fabrication. This PTFE film allows air/O<sub>2</sub> to flow from atmosphere to the electrocatalyst sites not the liquid across the film. The typical properties of methanol, ethanol and sodium borohydride are given in table (3.5). Potassium hydroxide was used as an electrolyte which was obtained from Fisher Scientific, India. Freshly prepared distilled water was used in all the experiments. Molten wax and Teflon tape were used for leakage prevention.

**Table 3.2 Typical Properties of Carbon paper**

<b>Toray Carbon paper, TGP-H-60</b>	
<b>Typical properties</b>	<b>Value</b>
Thickness	0.19 mm
Bulk density	0.44 g/cm <sup>3</sup>
porosity	78 %
Surface roughness	8 μm
Electrical resistivity through plane in plane	80 mΩcm
Thermal conductivity	
Through-plane (room temperature)	1.7 W/(m.k)
In-plane (room temperature)	21 W/(m.k)
In-plane (100 °C)	23 W/(m.k)
Coefficient of thermal expansion in plane (25~100 °C)	-0.8
Flexural strength	40 Mpa
Flexural Modulus	10 GPa
Tensile strength	50 N/cm

**Table 3.3 Ingredients of Nafion<sup>®</sup> solution (Grade: D-520)**

Sr. No.	Solution Components	Wt. %
1	Polymer content	5.0 min – 5.4 max
2	Water content	45 ± 3
3	VOC Content	50 ± 3
	1-propanol	48 ± 3
	Ethanol	< 4
	Mixed ethers and other	< 1
	VOCs	
4	Specific Gravity	0.92-0.94
5	Available Acid Capacity (meq/g, H <sup>+</sup> polymer basis)	> 1
6	Total Acid Capacity (meq/g, H <sup>+</sup> polymer basis)	1.03-1.12
7	Viscosity (cP; at 25°C and 40 sec <sup>-1</sup> Shear Rate)	10-40

**Table 3.4 Properties of PTFE Dispersion (Sigma Aldrich, USA)**

Sr. No.	Properties	Value
1	concentration	60 wt. % dispersion in H <sub>2</sub> O
2	particle size	0.05-0.5 $\mu\text{m}$
3	pH	10
4	viscosity	~20 cP (lit.)
5	transition temp	T <sub>m</sub> 337 °C (ASTM D 1457)
6	density	1.5 g/mL at 25 °C

**Table 3.5 Typical Properties of the fuels at 1.01 bar and 298 K**

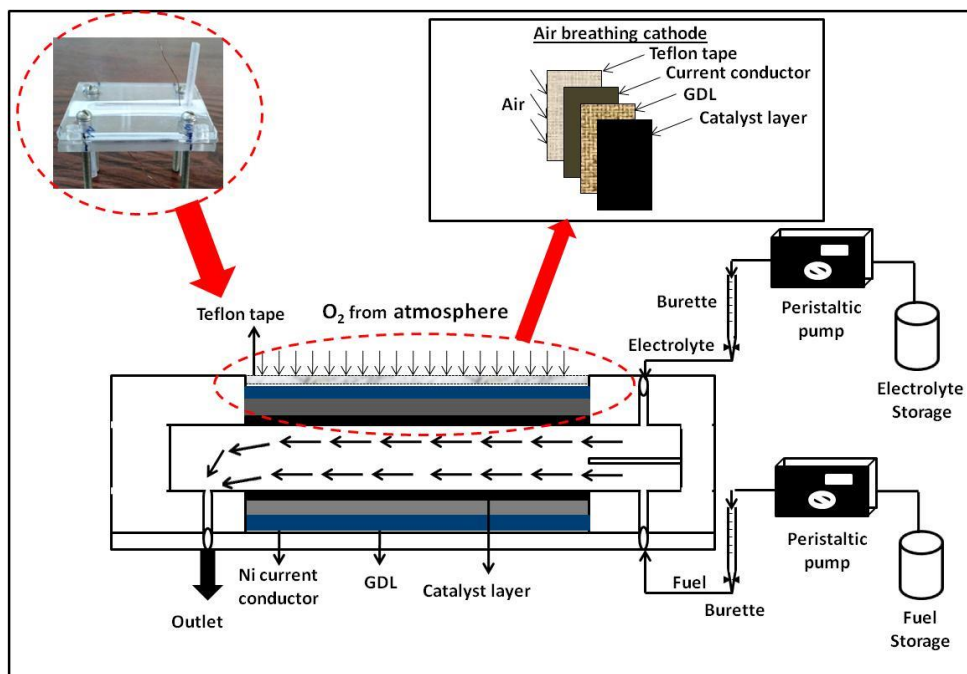
Reactant/Fuel	Molecular Formula	Mol. Wt.	E (KWh/Kg)	H (KJ/mole)	$\Delta G$ (KJ/Kg)
Methanol	CH <sub>3</sub> OH	32	6.09	-726.7	-702.7
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	46	7.44	-1367.9	-1326.7
Sodium Borohydride	NaBH <sub>4</sub>	38	7.00	-1932	-1239

Where E: Energy density; H: Enthalpy;  $\Delta G$ : Gibbs free energy of formation; E<sub>red.</sub>:  
Reduction voltage of half-cell

## 3.2 Experimental Setup

### 3.2.1 Air Breathing Microfluidic Fuel Cell

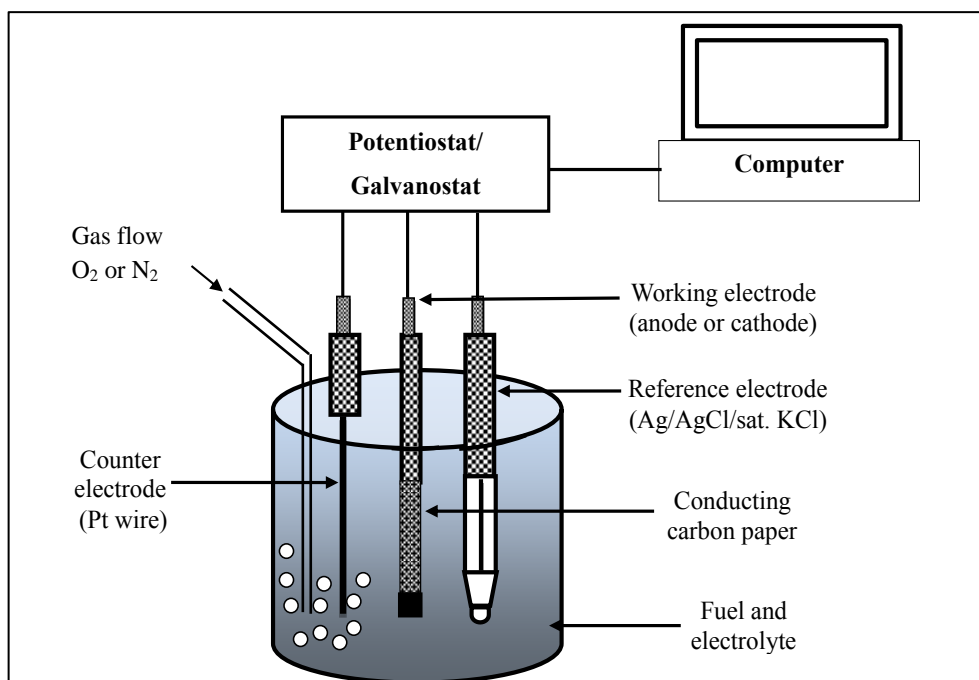
Air breathing microfluidic fuel cell tests were performed with a single cell design. Schematic of the experimental setup is shown in fig (3.1). The air breathing microfluidic fuel cell was fitted with  $0.9 \text{ cm}^2$  of anode and cathode, clamped between two Perspex sheets with the windows of 3 mm X 30 mm to fit the electrodes. The spacing between the windows is kept 0.9 mm. Molten wax was used on both sides of the window and electrodes for leakage prevention. The pressure at the anode and cathode was maintained at 1 bar. The mixture of fuel and electrolyte (KOH) of different concentrations were fed to the anode at a flow rate of 2.1 ml/min using a peristaltic pump (Electrolab) via burette. The air breathing cathode was exposed to ambient air for oxygen diffusion from atmosphere to the cathode side. The KOH of different concentrations was also fed to the cathode side at the flow rate of 0.9 ml/min using a peristaltic pump (Electrolab) via burette. In another experiment,  $\text{H}_2\text{O}_2$  mixed with varying concentrations of KOH were also supplied to the air breathing cathode side at a flow rate of 0.9 ml/min to check the effect of mixed oxidant ( $\text{H}_2\text{O}_2$  mixed with atmospheric air). The current and voltage data were recorded using multimeters (Sanwa, Japan) for different fuel (methanol or ethanol or sodium borohydride) concentrations, electrolyte (KOH) concentrations, and various oxidant ( $\text{H}_2\text{O}_2$ ) concentrations. The cell was operated at varying temperature irrespective of variation in other conditions. The photograph of the air breathing microfluidic fuel cell set up is given in appendix A1 (Fig A1.a).



**Figure 3.1** Schematic of the experimental setup of an air breathing microfluidic fuel cell.

### 3.2.2 Half-Cell Studies

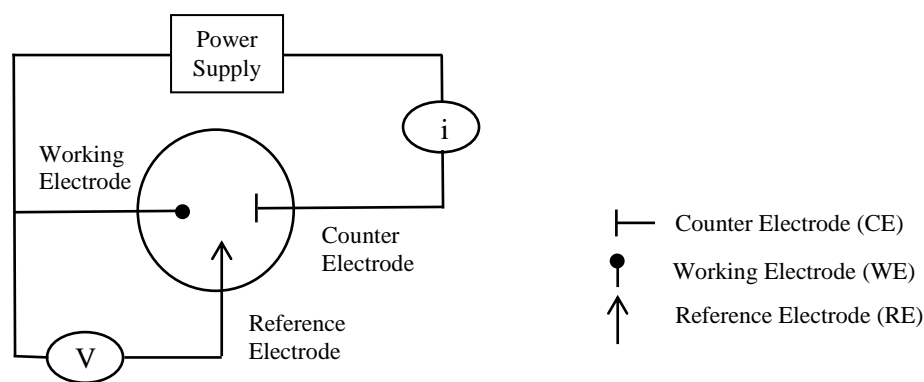
Single electrode studies of the individual anode and the cathode as used in the fuel cell tests were performed using cyclic voltammetry (PGSTAT 204, Autolab Netherland). The working electrode was prepared from a long strip of commercial carbon paper whose tip was coated with the electrocatalyst. The rest of the strip connected to the outside circuit. The cathode was immersed in the oxygen saturated electrolyte of varying concentration or varying concentration of  $\text{H}_2\text{O}_2$  mixed with KOH in the presence of purged oxygen. Whereas, the anode was immersed in the fuel and electrolyte solution of different concentrations saturated with nitrogen gas. Nitrogen was used to maintain an inert atmosphere. Nitrogen or air was supplied from the gas cylinder and purged through the solution using silicon tubing.



**Figure 3.2** Schematic of cyclic voltammetry setup for single electrode studies.

The terminals of the electrodes were connected to a Potentiostat-Galvanostat (PGSTAT 204, Autolab Netherland) for cyclic voltammetry results. The potentiostat is an electronic instrument consist of three electrodes, e.g., working (anode or cathode), counter (Pt wire) and reference (Ag/Agcl/Sat. KCl) electrodes (Fig 3.2). The potentiostat was connected to a computer which recorded all current-voltage data and NOVA 1.10 software was used to generate the voltammograms. The potentiostat has control of voltage and current across working electrode (WE) and counter electrode (CE), and it adjusts this V/I to maintain the potential difference between the working electrode and a reference electrode (RE), which is high impedance loop. Current is passed between CE and WE and the potential of the working electrode is monitored w.r.t reference electrode (Fig 3.3).





**Figure 3.3** Three electrode cell and notation for the different electrodes (Bard and Faulkner 2001).

### 3.3 Method

#### 3.3.1 Preparation of Carbon Cloth/Gas Diffusion Layer (GDL)

The carbon cloth/gas diffusion layer (GDL) was prepared from a mesh like cotton cloth. The ink of high surface area ( $75 \text{ m}^2/\text{g}$ ) carbon black (acetylene) was prepared by dispersing carbon black of loading  $1.0 \text{ mg}/\text{cm}^2$ , a mixture of isopropanol and Nafion<sup>®</sup> dispersion and PTFE dispersion a few drops, which acts as a binder. The ink/slurry was made by dispersing the components with the help of an ultrasonic water bath for 30 min. The half of the slurry was uniformly spread on the one side of the cotton cloth in the form of a continuous wet film using a brush. The remaining half of the slurry was spread on the other side of the cotton cloth. It was then dried in a vacuum oven for 1 h at  $80 \text{ }^\circ\text{C}$ . The dried carbon cloth was hot pressed at a pressure of  $10 \text{ kg}/\text{cm}^2$  for 2 min and then sintered at  $300 \text{ }^\circ\text{C}$  for 3 h to obtain the final form of the carbon cloth or GDL (Rathoure et al., 2016). The area specific resistance of the GDL was in the order of  $10 \text{ } \Omega \text{ cm}^2$ . It should be noted that only in some experiments IIT (BHU) laboratory developed GDL was used as substrate

for electrode fabrication. Until unless it is mentioned, in all experiments commercial GDL was used for electrode fabrication.

### **3.3.2 Electrode Preparation**

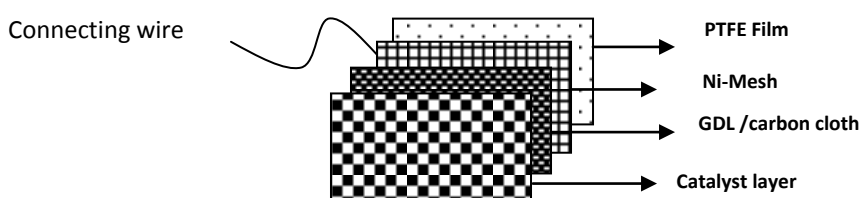
#### **3.3.2.1 Anode**

The anode for air breathing microfluidic fuel cell should be porous in nature to ensure liquid fuel (methanol or ethanol or sodium borohydride) diffusion through the anode active zones. The anode was prepared by dispersing the required quantity of electrocatalyst, and a mixture of Nafion<sup>®</sup> ionomer and PTFE dispersion, which acted as binders. PTFE, along with pores at the electrode provides a flow network, which allows easy escape of the reaction products from the electrodes. For the anode fabrication, Toray Carbon Paper/GDL and (Alfa Aesar, USA) in some cases IIT (BHU) laboratory made carbon cloth was first hot pressed to the Ni-mesh, which serves as current collector. The anode electrocatalyst slurry was then prepared by dispersing the required quantity of electrode electrocatalyst powder in Nafion<sup>®</sup> solution with a few drops of PTFE dispersion for 30 min using an ultrasonic water bath. The slurry was then uniformly spread on the GDL in the form of a continuous wet film using a brush. It was then dried in an oven for 1 h at 80 °C to form a porous solid anode. The dried electrode was sintered at a temperature of 300 °C for 3 h to obtain the final form of the electrodes. The area of the anode was in the order of 0.9 cm<sup>2</sup> (3 mm X 30 mm).

#### **3.3.2.2 Preparation of Air Breathing Cathode**

The air breathing cathode fabrication of microfluidic fuel cell is very crucial to maintain three phase (gas, liquid and solid) contact for efficient mass transfer from bulk phase (air)

to the electrocatalyst sites, i.e., active zones of the electrode. The cathode electrocatalysts ink was prepared using similar methods as for the anode. First of all three layers, air breathing composite was made from laboratory made carbon cloth or commercial carbon, Ni- mesh as a current collector and air breathing extreme outer layer PTFE film. The GDL and Ni- mesh was hot pressed at a pressure of  $10 \text{ kg/cm}^2$  for 2 min keeping the temperature at  $90 \text{ }^\circ\text{C}$ . The outer layer of the Ni-mesh was covered with a PTFE film and further hot pressed using similar conditions.



**Figure 3.4** Four layers composite of an air breathing cathode.

The GDL side of the three layers composite was painted by cathode catalyst ink using a paintbrush. It was then dried in an oven for 1 h at  $80 \text{ }^\circ\text{C}$  to form a porous solid anode. The dried cathode was sintered at  $300 \text{ }^\circ\text{C}$  for 3 h to obtain the final form of the electrodes (Fig 3.4). The area of the cathode was same, in the order of  $0.9 \text{ cm}^2$  (3 mm X 30 mm).

### 3.3.2.3 SEM of Electrodes

The sintered electrodes (anode and cathode) of different loading were visually observed in scanning electron microscope (SEM) to determine the surface morphology of the electrodes and GDL are shown in chapter 5 in result and discussion section 5.1 (Page no. 93)

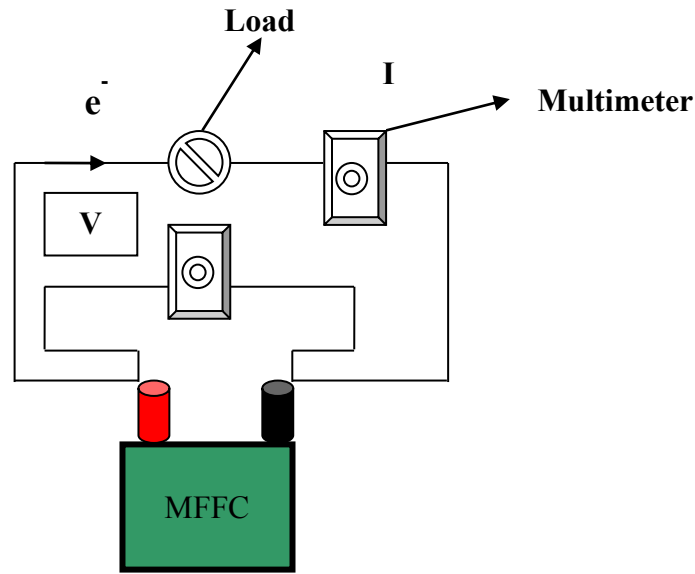
### 3.3.2.4 Half-cell Analyses Using Potentiostat

Prepared electrodes were tested to study the electrochemical reaction behavior/kinetics and to verify the reaction mechanism as reported in the different published literature (Rathoure et al., 2016, Pramanik et al., 2017 and Pandey et al., 2009). Using cyclic voltammetry experiments in a three electrode cell assembly (Fig 3.2) connected to a potentiostat. The working electrodes are the anode or cathode to be tested. The working of the potentiostat has already been explained in the previous section 3.2.2 (Page no. 61). The electrooxidation mechanism of the anode fuels (methanol, ethanol, and NaBH<sub>4</sub>) were systematically studied using three electrodes dipped into the mixture of methanol and KOH or ethanol and KOH or NaBH<sub>4</sub> and KOH solution. The solution mixture was saturated with nitrogen gas by passing nitrogen gas for 30 min. The oxygen reduction mechanism was studied with the cathode and using electrolyte saturated oxygen for 30 min. The experiments were conducted to study the effect of various parameters, e.g., scan rate, fuel concentration, electrolyte concentration and electrocatalyst loading for methanol or ethanol or NaBH<sub>4</sub> electrooxidation.

### 3.3.3 Air Breathing Microfluidic Fuel Cell

The air breathing microfluidic fuel cell was constructed with different anode and cathodes and tested under different operating conditions. The mixture of given concentrations of fuel (methanol, ethanol and sodium borohydride) and electrolyte KOH was fed to the anode at a flow rate of 2.1 ml/min using a peristaltic pump (Electrolab, India). Air breathing cathode was exposed to air for ambient oxygen diffusion to the cathode side. The electrolyte (KOH) of different concentrations was fed to the cathode at a flow rate of 0.9 ml/min. In another experiments, different concentrations of H<sub>2</sub>O<sub>2</sub> mixed with KOH were also fed to the air

breathing cathode side to check the effect of mixed oxidant ( $\text{H}_2\text{O}_2$  and air). The open circuit voltage (OCV) was measured with the help of multimeter (Fig 3.5). The voltage and corresponding short circuit current were measured at variable load condition to obtain current density vs. cell voltage (I-V) or polarization characteristics (Fig 3.5).



**Figure 3.5** Electrical circuit for measuring I-V characteristic curve data.

The steady state values of voltage and current were noted in all experiments. The effects of different parameters, e.g., fuel concentration, electrolyte concentration, oxidant concentration, temperature, electrocatalyst type and electrocatalyst loading on fuel cell performance were studied. Experiments were repeated to check the reproducibility of the data.

### **3.3.4 Lifetime Analysis of the Microfluidic Fuel Cell**

The lifetime of the air breathing microfluidic fuel cell was tested for different fuels (methanol, ethanol and sodium borohydride). The fuel cell terminals were connected with a fixed load. The cell voltages versus time data were noted down continuously for 11 hours.