

CHAPTER 3

EXPERIMENTAL

The materials used for the synthesis of electrocatalyst, electrode manufacturing and microfluidic fuel cell fabrication are discussed in the section 3.1 Materials below. The detailed method used for the manufacturing of electrocatalysts, electrocatalyst characterization and single microfluidic fuel cell are discussed in the section 3.2 Method.

3.1 Materials

The acetylene black carbon (C_{AB}) as support material was used to synthesize Pd-Pt/C and Pd-Ni/C anode electrocatalysts for glycerol electrooxidation. The support material, C_{AB} was procured from Alfa Aesar, USA. Glycerol (Fisher Scientific, India) (Table 3.1) was used as fuel and KOH (Fisher Scientific, India) as electrolyte. The precursors for electrocatalyst preparation were $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$ and $NiCl_2 \cdot 6H_2O$ (Alfa Aesar, USA) for the metal Pt, Pd and Ni, respectively. The cathode electrocatalyst was commercial Pt (40 wt. %)/ C_{HSA} (Alfa Aesar, USA). The gas diffusion layer (GDL) (TGP-H-60, Alfa Aesar, USA) was used as substrate for the depositing electrocatalyst ink (Table 3.2). The Nafion[®] dispersion (D-520, 5 wt. %, Alfa Aesar, USA) was used to prepare the electrocatalyst ink and also to make the electrocatalyst layer conducting for ions (Table 3.3). Polytetrafluoroethylene (PTFE) dispersion (60 wt. %, Sigma Aldrich, USA) was used as binder for the electrodes (Table 3.4). A thin and flat Nickel mesh was used as current collector. Copper wire was used for internal connections to complete the circuit. Ambient oxygen/air was used as oxidant. The laboratory prepared distilled water was used in all the experiments. Teflon tape and molten wax were used for leakage prevention of MFC assembly. In some experiments mixture of calcium hypochlorite (Loba chemie Pvt Ltd, Mumbai, India) and oxygen from air was used as mixed oxidant.

Table 3.1 Properties of glycerol fuel (Fisher scientific, India).

Sr. No.	Properties	Value
1	Molar mass (g/mol)	92
2	Relative density (Kg/m ³)	1260
3	Melting point (°C)	18
4	Boiling point (°C)	290
5	Flash point (°C)	160
6	pH	5

Table 3.2 Properties of Toray Carbon paper, TGP-H-60 (Alfa Aesar, USA).

Sr. No.	Properties	Value
1	Thickness (mm)	0.19
2	Bulk density (g/cm ³)	0.44
3	Porosity (%)	78
4	Surface roughness (μm)	8
5	Electrical resistivity through plane in plane ($\text{m } \Omega \text{ cm}$)	80
6	Thermal conductivity (W/(m.k))	1.7
7	Through-plane (room temperature) (W/(m.k))	21
8	In-plane (room temperature) In-plane (100 °C) (W/(m.k))	23
9	Coefficient of thermal expansion in plane (25~100 °C)	-0.8
10	Flexural strength (Mpa)	40
11	Flexural Modulus (Gpa)	10

Table 3.3 Composition and properties of Nafion[®] solution (Alfa Aesar, USA).

Sr. No.	Nafion [®] solution details	Components/properties of Solution	Value
1	Solution components (Wt. %)	Polymer content	5.0 min – 5.4 max
		Water content	45 ± 3
		VOC Content	50 ± 3
		1-propanol	48 ± 3
		Ethanol	< 4
		Mixed ethers and other VOCs	< 1
2	Solution properties	Specific Gravity	0.92-0.94
		Available Acid Capacity (meq/g, H ⁺ polymer basis)	> 1
		Total Acid Capacity (meq/g, H ⁺ polymer basis)	1.03-1.12
		Viscosity (cP; at 25 °C and 40 per second Shear Rate)	10-40

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

Sr. No.	Properties	Value
1	Concentration (wt. % dispersion in H ₂ O)	60
2	Particle size (μm)	0.05-0.5
3	pH	10
4	Viscosity (cP (lit.))	~20
5	Transition temperature (ASTM D 1457)	337 °C
6	Density (g/mL at 25 °C)	1.5

3.2 Method

3.2.1 Bimetallic Pd-Pt/C electrocatalyst synthesis

Acetylene black carbon (C_{AB}) supported Pd (20 % by wt.) and bimetallic Pd-Pt with varying Pd to Pt weight ratio of 16:4, 10:10, 4:16 electrocatalysts with low metal loading of 20 wt. % on 80 wt. % were synthesized using impregnation reduction method (Tayal et al., 2011). At first, the suitable amount of metal precursors i.e., $PdCl_2$ and $H_2PtCl_6 \cdot 6H_2O$ based on different ratios were dissolved in isopropanol separately by ultrasonic treatment for 30 min. Then acetylene black carbon preheated at 110 °C was poured into the warm precursor solution and continuously stirred till smooth and thick slurry was achieved (Panjiara and Pramanik 2021b). Then it was kept overnight for drying at room temperature. Further, the slurry was dried at 110 °C and ground into powder by an agate mortar. The ground electrocatalyst powder was reduced in a continuous hydrogen supply environment, keeping the sample in a tubular furnace at 120 °C for 2 h and finally it was cooled to room temperature. The final form of the synthesized electrocatalyst i.e., Pd/C, Pd-Pt (16:4)/C, Pd-Pt (10:10)/C and Pd-Pt (4:16)/C were then sent for physical and electrochemical characterization.

3.2.2 Bimetallic Pd-Ni/C electrocatalyst synthesis

Similarly, Pd-Ni/C bi-metallic electrocatalyst of different metal ratios of Pd and Ni such as 16:4, 10:10 and 4:16 were prepared using acetylene black carbon (C_{AB}) support by the impregnation reduction method as discussed in the previous section. The electrocatalyst was prepared with 80 wt. % support material and 20 wt. % total metal (Pd-Ni) loading. At first, the required amount of precursors i.e., $PdCl_2$ and $NiCl_2$ were dissolved in the solvent isopropanol using ultrasonic treatment for 30 min. The preheated acetylene black carbon at 110 °C was mixed slowly into the solution of the precursor followed by heating using magnetic hot plate stirring until the solvent become smooth and thick slurry.

Further, the thick slurry was kept for air drying overnight followed by another drying for 1 h in an oven at a temperature of 110 °C. The dried electrocatalyst powder was properly mixed in a mortar and then reduced by hydrogen flow in a glass tube. The glass tube was fixed in a tubular furnace at a heating temperature of 200 °C for 2 h. Finally, the prepared electrocatalyst powder of various metal ratios were designated as Pd-Ni (16:4)/C, Pd-Ni (10:10)/C and Pd-Ni (4:16)/C which were left to cool at room temperature for further physical and electrochemical characterization. The synthesis of single metal based electrocatalyst Pd (20 wt. %)/C has already been discussed in previous section.

3.2.3 Physical characterization of electrocatalyst

3.2.3.1 X-ray diffraction (XRD)

The crystallographic analyses of synthesized supported electrocatalysts supported on acetylene black carbon were investigated by X-ray diffraction (XRD) technique (Rigaku Ultima IV, Germany). The XRD diffractometer containing nickel filtered Cu K α radiation source ($\lambda=0.154056$ nm) was used to produce the XRD patterns which was maintained at 40 kV tube voltage and 15 mA tube current. The electrocatalyst sample of 30 mg was taken to obtain a uniform distribution of the sample. The 2θ range of diffraction angles were varied from 20° to 90° at a scan rate of 5° min⁻¹ with a 0.02° angular resolution.

3.2.3.2 Scanning electron microscopy (SEM)/ Energy dispersive X-ray spectroscopy (EDX)

The surface morphology of the synthesized acetylene black carbon supported electrocatalysts were examined by scanning electron microscopy (SEM) (Nova Nano SEM 450, FEI Company U.S.A). The elemental composition at the surface of the electrocatalyst was investigated by energy dispersive X-ray spectroscopy (EDX) using Octane Plus SDD detector (EDAX Inc.) attached with SEM instruments. The SEM image gives information about surface morphology of the supported electrocatalyst and

electrocatalysts distribution over support material. While, the approximate surface composition can easily calculated from EDX analysis.

3.2.3.3 Transmission electron microscopy (TEM)

The particle size distributions of synthesized acetylene black carbon supported electrocatalyst were obtained from transmission electron microscopy (TEM) analyses (Tecnai G2 20 Twin, FEI Company, USA). The samples for TEM analyses were prepared by dispersing the synthesised electrocatalyst in ethanol solvent using in ultrasonic water bath. The electrocatalyst sample was applied on carbon coated Cu grid using a micro pipette. The sample grid was then dried in a vacuum oven at 60 °C for 4 h and then it was used for analysis by TEM.

3.2.4 Electrochemical characterization of electrocatalyst

3.2.4.1 Cyclic voltammetry (CV) analysis

The electrochemical activity of the synthesized anode electrocatalysts for the electrooxidation of glycerol was performed by cyclic voltammetry (CV). The CV comprises of three electrode cell assembly (PGSTAT 204, Autolab Netherland) as shown in Figure 3.1. The three electrodes are working electrode, counter electrode and reference electrode, respectively. A long platinum wire was used as counter electrode. The Ag/AgCl in saturated KCl was used as reference electrode. The working electrode was prepared by coating synthesized anode electrocatalyst on one end of a strip of carbon paper/GDL (Table 3.2) The electrocatalyst ink was prepared in a similar way and using same composition for both anode and cathode electrode, except the electrocatalyst. The method of electrocatalyst ink preparation is discussed in the next section “3.2.5 Electrode preparation” (page no. 53). The prepared electrocatalyst ink was uniformly painted with the help of paint brush on the tip of a long strip of carbon paper of 0.5 cm² geometrical area in single side. All the electrochemical measurements were performed in an alkaline

medium containing 1 M KOH and 1 M glycerol. The dissolved O_2 in the prepared solution creates hindrance for the glycerol electrooxidation, thus it was removed from the electrolyte solution by purging nitrogen gas for 30 min before start of each experiment.

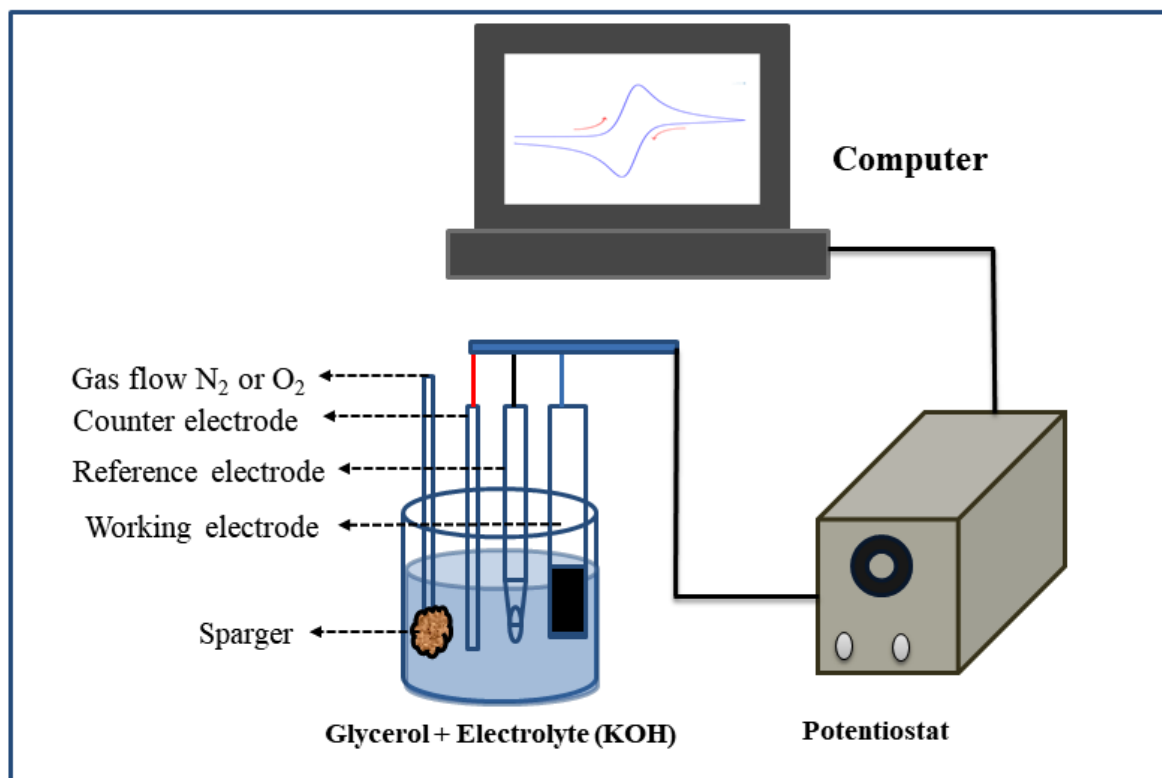


Figure 3.1 Schematic of three electrode cell assembly for performing CV and EIS studies with the help of potentiostat galvanostat (PGSTAT).

3.2.4.2 Electrochemical impedance spectroscopy (EIS) study

The EIS is a valuable technique to find out the charge transfer resistance or ionic conductivity of interfaces and various layers adjacent to the electrode surface. Here in the thesis, the aim of the EIS analysis is to find out the charge transfer resistance of the electrode. The EIS analysis was performed at a frequency range of 100 kHz to 10 mHz with amplitude of 10 mV at the anodic peak potential V (vs Ag/AgCl) of electrocatalyst obtained from cyclic voltammograms. The arrangements of all three electrodes were similar as that of CV analysis (Figure 3.1).

3.2.5 Electrode preparation

The anode electrodes were fabricated using synthesized electrocatalysts and the commercial Pt (40 wt. %)/C_{HSA} was used for the cathode preparation. The electrocatalyst slurry was made by taking the desired amount of electrocatalyst, acetylene black carbon with a few drops of Nafion[®] (Table 3.3) and PTFE dispersion (Table 3.4) in isopropanol as a solvent followed by ultrasonication for 30 min. The PTFE dispersion restricts the flooding on the electrode surface. The anode and cathode electrocatalyst ink composition were similar, except the electrocatalyst used at anode and cathode as mentioned above. It should be noted that anode was made of three layers and cathode of four layers composite, respectively. To make three layers anode, the GDL and Ni mesh was hot pressed at a temperature of 70 °C and 10 kg/cm² of pressure for 1 min followed by anode electrocatalyst ink painting using a paint brush uniformly over the GDL. The electrocatalyst layer was dried in an oven for 1 h at a temperature of 80 °C. The dried three layer anode was sintered at a temperature of 280 °C for 3 h. The four layer cathode was made by hot pressing using same condition as used for anode keeping the Ni mesh in between GDL and an air diffusion PTFE layer. The cathode electrocatalyst ink was painted over the GDL followed by drying and sintering the four layers composite at same conditions of anode manufacturing. The flow profile of anode and cathode stream is shown in Figure 3.2. The flow direction of glycerol is in the axial direction and it is direct contact with the electrocatalyst surface. While, the atmospheric oxygen diffuses in the radial direction and passes through PTFE layer, nickel mesh and GDL to reach the cathode electrocatalyst layer.

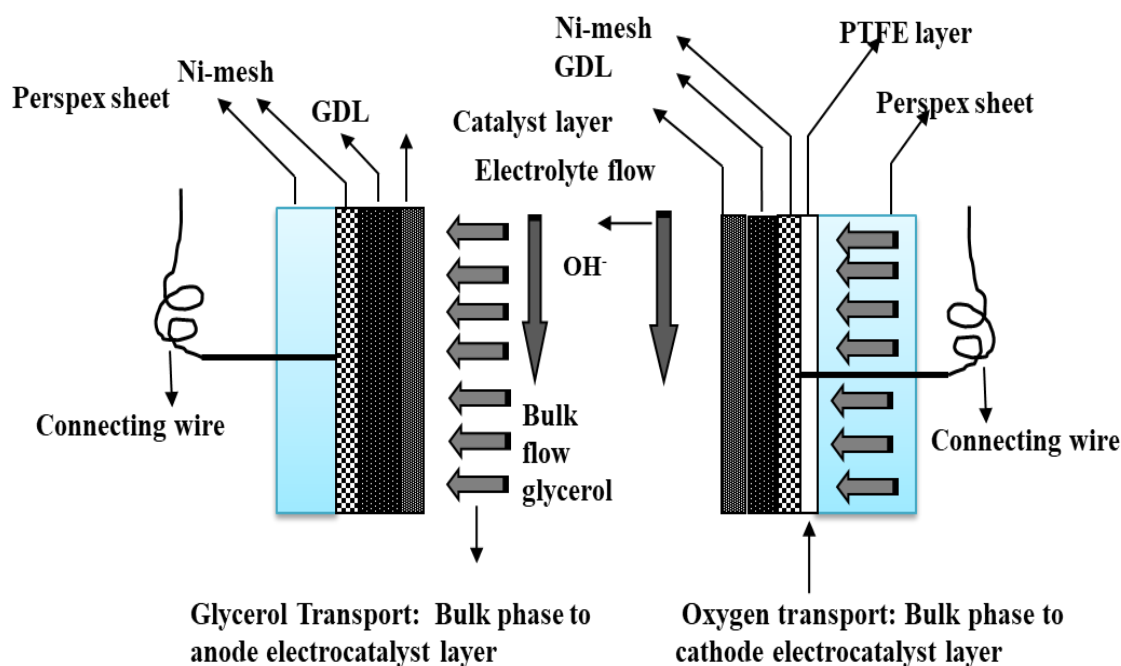


Figure 3.2 Glycerol transport pathway from bulk phase to the anode electrocatalyst layer and oxygen transport pathway from ambient to the cathode electrocatalyst.

3.2.6 Experimental setup

As already discussed, two types of air breathing microfluidic fuel cell were fabricated to study the electrooxidation of glycerol fuel using synthesized electrocatalyst. The experimental setups of Y-shaped and T-shaped are discussed in the following section.

3.2.6.1 Y-shaped air breathing microfluidic fuel cell

A novel design of Y-shaped air breathing MFC was fabricated in the laboratory as shown in Figure 3.3a. The Y-shaped air breathing MFC was fabricated using PMMA (poly methyl methacrylate) sheets purchased from Varanasi (India) (Table 3.1). The microchannel was fabricated using CNC mill production with simulator (EMCO Concept MILL 260, EMCO Maier) machine at IIT (BHU). The MFC consists of two PMMA sheets with dimension of 90 mm × 70 mm × 5 mm (length × width × height). The Y-shaped channel was machined on the top layer of bottom plate with two arms/channel of

Y-shape having dimensions of 20 mm × 1 mm × 2 mm (length × width × height) separated with 90° angle. The ends of two arms/channels were connected to two inlet tubes. One inlet arm/channel for fuel and electrolyte mixture and the other one for electrolyte solution were used. The main microchannel of dimension 30 mm × 1 mm × 2 mm was connected at the junction of two arms to form the Y-shaped MFC. The electrodes were fixed to the wall of the main channels with effective surface area of the electrode of 0.6 cm² (30 mm × 2 mm). The oxidant air/oxygen was diffusing from outside channel to the bulk of the catholyte through the air passage as shown in the Figure 3.3a. The enlarged and detailed internal view of Y-shaped air breathing microfluidic fuel cell main unit is shown in the Figure 3.3b. The end of the main channel was attached with an outlet hole of 1 mm diameter for the discharge of reaction products, unreacted glycerol, oxidant and electrolyte. The Y-shaped microchannel was covered with the other PMMA sheet. The sealing was done by keeping PTFE tape between two PMMA sheets for eliminating any short of fuel and electrolyte leakage. Finally, the assembly of two PMMA sheets were clamped by six bolts of 3 mm diameter. Nickel mesh was used as current collector because it has corrosion resistance to alkaline medium. The electrocatalyst side i.e., inner side of anode and cathode is direct contact with the fuel and electrolyte streams, respectively. While, the outer side was connected with copper wire as external connection to complete the circuit. The anode stream was different glycerol concentration mixed with KOH solution and cathode stream was KOH solution with atmospheric air as oxidant. Both anode and cathode streams were supplied with varying flow rates ranging from 0.3 ml/min to 1.5 ml/min to obtain the optimum flow rates. The solutions were supplied using peristaltic pump whose outlet was connected to a burette to maintain the liquid head and inlet flow at anode and cathode streams, respectively. The voltage current (V-I) data were collected using multimeters (RISH-14, India) to get polarization characteristics of MFC.

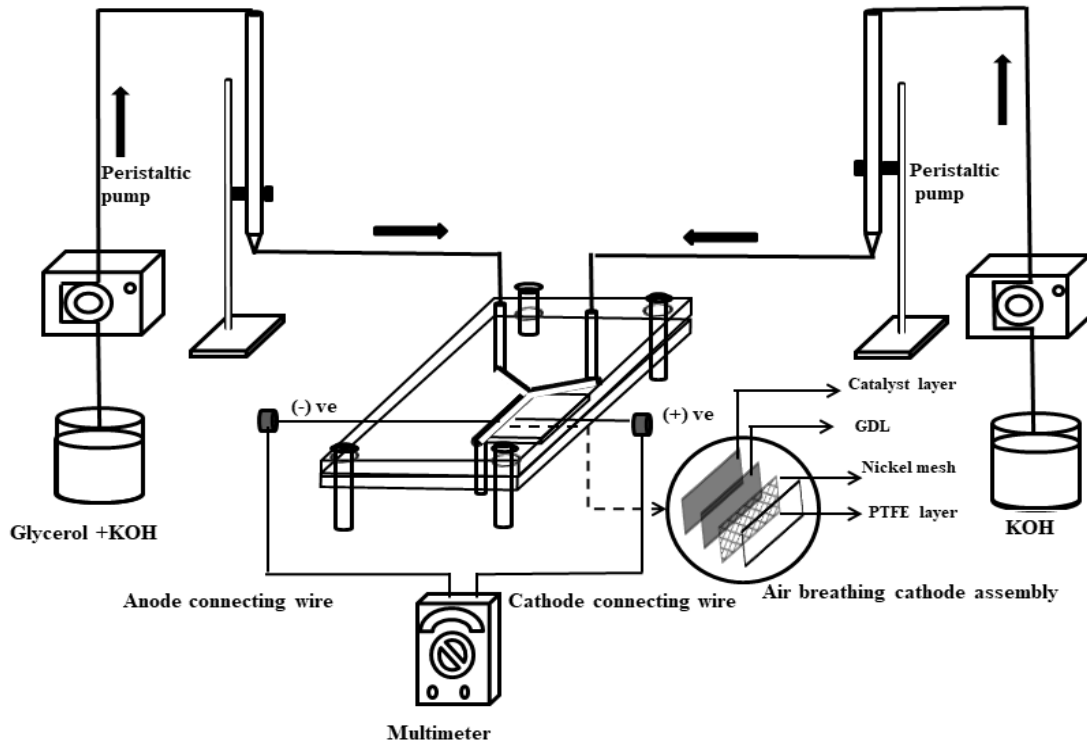


Figure 3.3a Schematic of Y-shaped air breathing microfluidic fuel cell setup.

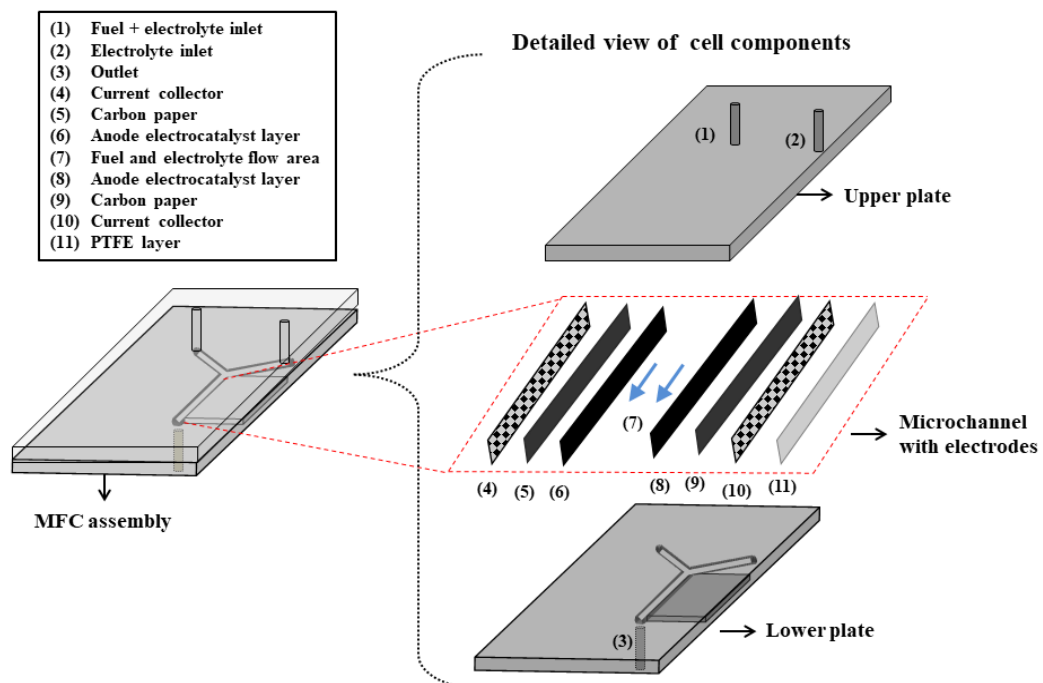


Figure 3.3b Enlarge and detailed internal view of Y-shaped air breathing microfluidic fuel cell main unit.

The electrolyte of 0.5 M KOH was fed to the microchannel channel at air breathing cathode side at same flow rate as used in anode. The actual photograph of the experimental setup is shown in Appendix A (Figure A1).

3.2.6.2 T-shaped air breathing microfluidic fuel cell

The T-shaped air breathing MFC was fabricated in the laboratory (IIT-BHU, India). The PMMA/perspex (poly methyl methacrylate) sheets purchased from Varanasi (India) was used to fabricate the T-shaped air breathing MFC. The grooves and microchannel was made using CNC mill production with simulator (EMCO Concept MILL 260, EMCO Maier) machine at IIT (BHU) similar to Y-shaped air breathing MFC discussed in the previous section. The T-shaped MFC device was made by the assembly of perspex sheet layers/windows as shown in Figure 3.4a to Figure 3.4b. The upper layer is for anode and lower layer is for cathode electrodes, whereas the middle layer is the flow channel for anode and cathode streams. The upper and lower PMMA sheets of 45 mm × 30 mm × 3 mm (length × width × height) dimension was taken for the fabrication of anode and cathode electrode holder. At first, a 32 mm × 5 mm channel was dissect in the middle of the PMMA sheet of above mentioned dimension, then a groove of 1 mm × 1 mm was fabricated inside the 32 mm × 5 mm channel for the proper fitting of electrode and current collector (Ni mesh) for the upper PMMA sheet. Two holes of 1 mm diameter were drilled in the both width side of 32 mm × 5 mm channel for inlet and one hole at the other end for outlet stream, respectively. The two inlet tubes vertical to channel was attached. One inlet arm was used for anode stream and other one for cathode stream. The outlet tube was attached at the end of the main channel for the discharge of reaction products. The middle PMMA sheets/spacer of 45 mm × 30 mm × 0.9 mm (length × width × height) dimension was taken for the flow channel fabrication of anode and cathode streams. A separator of 5 mm × 3 mm dimension was fixed at the entry point of

the flow channel to avoid the direct contact of anode and cathode streams. Finally, all the three layers of PMMA sheet were assembled by sealing with PTFE tape in between the three perspex sheets windows to prevent any short of fuel and electrolyte leakage. The three layer of PMMA sheets were fixed and tighten by four bolts of 3 mm diameter at four sides as shown in Figure 3.4a.

The prepared anode and cathode electrodes were fitted on the PMMA sheets windows. The area of electrodes was 0.9 cm^2 ($3 \text{ mm} \times 30 \text{ mm}$) for the placement of anode and cathode and the gap between electrodes was 0.9 mm. The internal detail of cell component of the single cell unit is shown in the Figure 3.4b. The inner side of anode and cathode with electrocatalyst layer is contact with anode and cathode stream, whereas the outer layers are connected with connecting copper wire. The bare portion of the anode electrode was covered with molten wax to stop the diffusion of oxygen from air to anode active zones. Similarly, air breathing cathode was fitted in another PMMA window keeping the PTFE coated side exposed to atmosphere and active electrocatalyst side in contact with cathode stream, so that oxidant oxygen can diffuse from atmosphere to cathode active zones. The internal details of the air breathing cathode i.e., four layer composite and three layer anode composite with anode and cathode stream flow is shown in Figure 3.4b. The different concentration of glycerol mixed with KOH as anode stream and different KOH concentration were supplied at varying flow rate ranging from 0.5 ml/min to 1.2 ml/min to get the optimum flow rates for both anode and cathode side, respectively. The anode and cathode stream were fed to the channel using a peristaltic pump (Electrolab, India) via vertical burette to reduce fluctuation of flow in the channel and maintain constant flow rate of the stream. The voltage and current (V-I) data were recorded using multimeters (Rish, India) to understand the polarization behaviour of the MFC. The actual image of the experimental setup is shown in Appendix A (Figure A2).

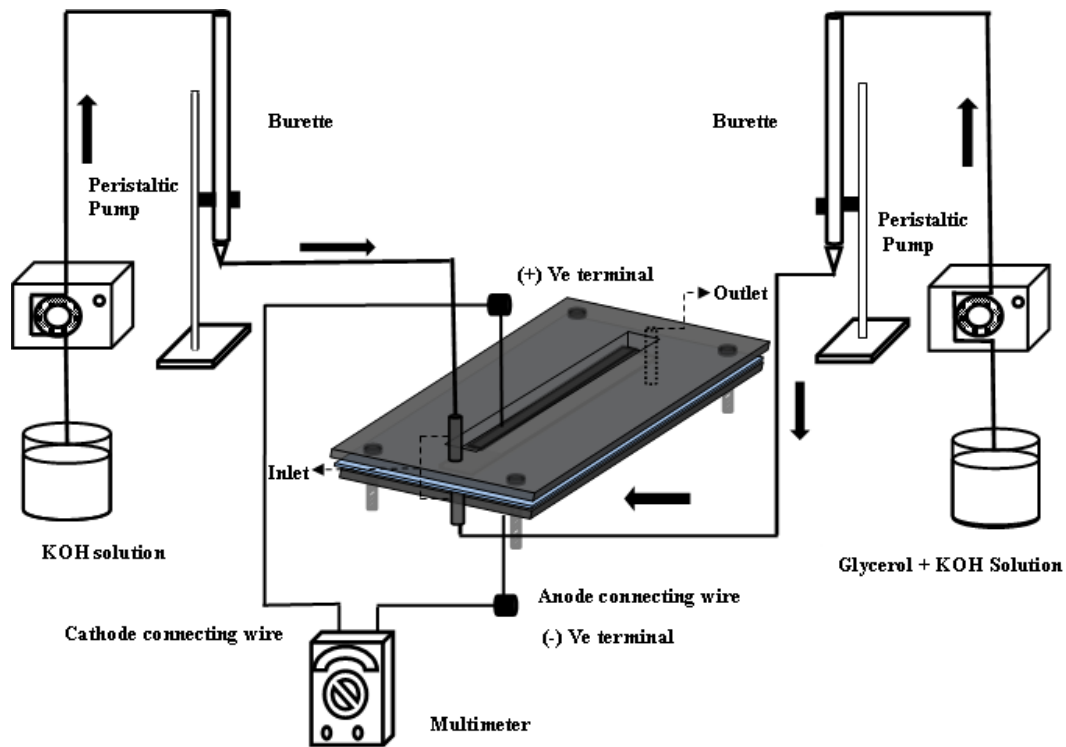


Figure 3.4a Schematic of T-shaped air breathing microfluidic fuel cell experimental setup.

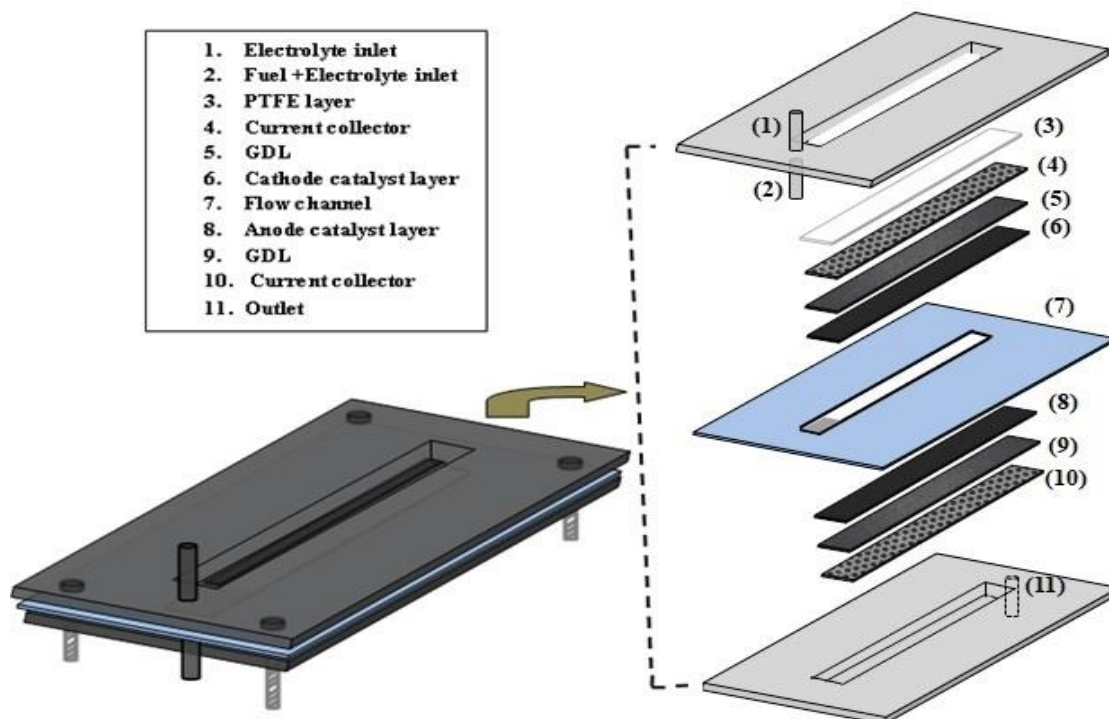


Figure 3.4b Enlarge and detailed internal view of T-shaped air breathing microfluidic fuel cell main unit.

3.3 Evaluation of dimensionless numbers in MFC

In the MFC operation, intermixing of fuel and oxidant and the stability of the liquid-liquid interface are the key factors controlling MFC performance. The intermixing of fuel and oxidant and the stability of the liquid-liquid interface in a microchannel depends upon the Reynolds Number (Re), Peclet number (Pe) and Schmidt number (Sc), respectively. All these three dimensionless numbers were calculated at various flow rates to maintain the dimensionless number within the permissible range.

The Reynolds number (Re) = $\frac{D_h V \rho}{\mu}$, where D_h is the hydraulic diameter of the channel, V is the average velocity, ρ is the density and μ is the viscosity of the stream. Reynolds number is the ratio of inertia force to viscous force and normally describes the nature of flow of liquid ($Re < 2100$ for laminar flow and $Re > 2100$ turbulent flow) (Kjeang et al., 2009). In microfluidic devices the Re is less than 1 and upto 100 (Banerjee et al., 2019). The laminar flow with low Reynolds number implies parallel flow of fluids without convective mixing.

The Schmidt number (Sc) = $\frac{\mu}{\rho D}$ is the ratio of molecular diffusivity to momentum diffusivity, where μ is viscosity, ρ is the density and D is diffusivity of the species in the solvent (Kjeang et al., 2009). The $Sc > 1$ designates that viscous force effect is more than concentration effect, this confirm the concentration boundary layer to a linear velocity profile (Kjeang et al., 2009). Similarly, the degree of mixing during laminar flow depends upon the value of Peclet number (Pe) = $\frac{V D_h}{D}$, which is defined as the ratio of convection transport to diffusive transport, where V is the average velocity in the channel, D_h is the hydraulic diameter of the channel and D is the diffusion coefficient of glycerol in water (Kjeang et al., 2009). The hydraulic diameter of the microchannel is calculated using the formula $D_h = \frac{4A}{P}$, where A is the cross section area of the flow channel and P is the

wetted perimeter of the channel cross section. The densities of the anode and cathode streams were determined using specific gravity bottle at 35 °C. The viscosities of anode and cathode streams were measured using LVDV-II Pro Brookfield digital viscometer at 35 °C. The diffusion coefficient of glycerol in water of was taken from Perry's Chemical Engineers Hand Book. The detailed calculation of Re, Sc and Pe and their values at various flow rates are presented in the section "5.3 Evaluation of dimensionless number" (page no. 171- 175).

3.4 Stability test of air breathing MFC

The stability test of the Y-shaped and T-shaped air breathing microfluidic fuel cell were performed for the most active and best electrocatalyst in single cell studies. The optimum operating parameters were used for the stability test for both Y-shaped and T-shaped MFC. The operating cell voltages versus operation time data were noted at a fixed load given with the help of potentiometer (Figure 3.5). The power density of the MFC were calculated at the interval of 1 h upto 12 h to check the stability of MFC performance. It should be noted that the data were recorded for 12 h only due to safety issue.

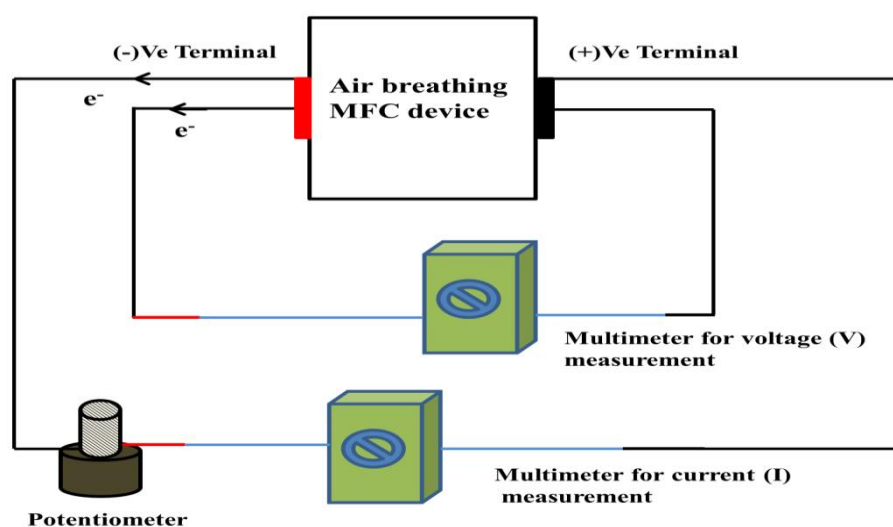


Figure 3.5 Schematic of electrical circuit connections for measuring voltage current (V-I) data.