CHAPTER 3

EXPERIMENTAL

This chapter deals with the materials needed to conduct the experiments and experimental details, related setups fabrication for electrochemical characterization and single cell DEFC studies, along with the manufacturing of various cell components and their performance study. As already discussed in the chapters introduction (Page no. 4) and literature review and objectives (Page no. 16, 22), electrode materials anode and cathode are the most active and important component of fuel cells. The synthesis and characterization of anode electrocatalysts were explored using different physical techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS), which are discussed in this section. Manufacturing and electrochemical characterization of anode electrodes using cyclic voltammetry (CV) and chronoamperometry (CA) techniques are also presented here in this chapter. The single DEFC study and stability are presented at the end of this chapter.

3.1 Materials

Hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6.6H_2O$) (99.9 % metal basis), ruthenium (III) chloride ($RuCl_3$) (48.2 wt. % Ru), and rhenium (III) chloride ($ReCl_3$) were obtained from Alfa Aesar, USA, and used as metal precursors for electrocatalyst synthesis. As a support material for synthesizing highly dispersed electrocatalysts, acetylene black (C_{PAB}) (S_{BET} surface area: 75 m^2/g, Alfa Aesar, USA) and multi-walled

carbon nanotubes (p-MWCNTs) (purity min. 95 %, diameter: 8-15 nm, length: 10-30 mm, specific surface area: 40-300 m^2/g, Sisco Research Laboratories Pvt. Ltd., India) were used. The commercial Pt-Ru (30 %: 15 % by wt.)/C electrocatalyst was obtained from Alfa Aesar, USA for comparison purposes. The commercial Nafion® 117 membranes (Alfa Aesar, USA) were used as solid electrolyte. The typical composition and properties of the commercial Nafion® 117 membranes (Alfa Aesar, USA) are shown in Table (3.1).

Table 3.1 Typical properties of the commercial Nafion® 117 membranes (Alfa Aesar, USA).

Typical properties	Values
Casting procedure	Extruded
Equivalent weight ($g_{polymer}$/mole$_{SO3H}$)	1100
ionic exchange capacity: meq$_{SO3H}$/g$_{polymer}$	≥ 0.90
Thickness (mm)	0.180
Surface resistance (Ω cm^{-2})	~ 0.09-0.12
Proton conductivity (S cm^{-1}) at 30 ℃ at 80 ℃	~10^{-2} ~0.10
Water absorption (wt. %)	~15
Specific Gravity	1.98

The Toray carbon paper (TGP-H-60, Alfa Aesar, USA) was used as a substrate or gas diffusion layer (GDL) for painting the electrocatalyst ink to fabricate the working electrodes used in half cell analysis and single cell DEFC tests. The GDL provides the support to the electrocatalyst layer after drying and helps to conduct electrons between flow channel and electrocatalyst layer. It also provides porous medium/path for transport

of ethanol fuel at anode and oxidant at cathode from bulk phase to the electrocatalyst layer. The typical composition and properties of the Toray carbon paper (TGP-H-60 Alfa Aesar, USA) are shown in Table (3.2).

Table 3.2 Typical properties of Toray carbon paper (TGP-H-60, Alfa Aesar, USA).

Typical properties	Values
Thickness (mm)	0.19
Bulk density (g/cm^3)	0.44
Porosity (%)	78
Surface roughness (μm)	8
Electrical resistivity through-plane in-plane (mΩcm)	80
Thermal conductivity Through-plane (room temperature) (W/(m.k)) In-plane (room temperature) (W/(m.k)) In-plane (100 ℃) (W/(m.k))	1.7 21 23
Coefficient of thermal expansion in plane (25-100 ℃)	-0.8
Flexural strength (MPa)	40
Flexural modulus (GPa)	10
Tensile strength (N/cm)	50

The Nafion® ionomer solution (D-520, 5 wt. %) was obtained from Alfa Aesar, USA, and used as an ionomer. The polytetrafluoroethylene (PTFE) dispersion (60 wt. %) was used as an electrocatalyst binder in minute amount and obtained from Sigma-Aldrich, Germany. The composition of Nafion® ionomer and PTFE dispersion are presented in Table (3.3) and Table (3.4), respectively.

Table 3.3 Composition and properties of Nafion® ionomer solution (Grade: D-520, Alfa Aesar, USA).

S. No.	Nafion® details	Type of components/properties	Values
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 others	< 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 ℃ and 40 per second shear rate)	10-40

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

S. No.	Properties	Values
1	Concentration (wt. %) dispersion in H_2O	60
2	Particle size (µm)	0.05-0.5
3	pH	10
4	Viscosity (cP) (lit)	~ 20
5	Transition temperature T_m (℃) (ASTM D 1475)	337 ℃
6	Density (g/ml) at 25 ℃	1.5

Nitric acid/HNO_3 (69-71 %, Fisher Scientific, India) and sulphuric acid/H_2SO_4 (min. 97

%, Fisher Scientific, India) were used for purification and functionalization of support

materials i.e., C_{PAB} and p-MWCNT. Ethylene glycol (99.0 %), formic acid/HCOOH (85 %) and isopropanol (99.5 %) were used as solvent and procured from Fisher Scientific, India. Perchloric acid/$HClO_4$ (70 %, Fisher Scientific, India) was used as electrolyte for half-cell studies. Ethanol was used as anode fuel (99.9 %, Merck, Germany). As a cathode oxidant, pure oxygen gas was used. A typical property of ethanol fuel is shown in Table (3.5). The commercial Pt (40 wt. %)/High surface area carbon (C_{HiSPEC}) (Alfa Aesar, USA) was used as cathode electrocatalyst. All experiments were performed with distilled water prepared in the laboratory, IIT (BHU).

Table 3.5 Typical properties of ethanol fuel at 1.01 bar and 298 K (**Lamy et al., 2001**).

Fuel	Molecular formula	Molecular weight	Energy density (kWh/kg)	Enthalpy of combustion (ΔH) (kJ/mole)	Gibbs free energy of formation (ΔG) (kJ/kg)
Ethanol	C_2H_5OH	46	8.01	-1367.9	-1326.7

According to the online shopping website "www.fuelcellstores.com", the basic cost of 50 g carbon Vulcan XC-72R power (product code 590106-1) is $ 50.00 (https://www.fuelcellstore.com). On the other hand, the cost of 250 g acetylene-black (C_{AB}) (product code 39724) is $ 56.00 (Alfa Aesar, USA). The cost analysis reveals that the acetylene-black cost ($ 0.224/g) is nearly a quarter of the carbon Vulcan XC-72R cost ($ 1.00/g). The typical properties of C_{AB} as well as the cost analysis in comparison to the Vulcan XC-72R support are presented in Table (3.6).

Table 3.6 Cost analysis and comparison of properties of the carbon support acetylene black with Vulcan XC-72R.

Type of carbon support	Manufacturer	Particle size (nm)	Surface area (m^2/g)	Cost of carbon support ($)	Unit cost of carbon support
Acetylene-black (C_{AB})	Alfa Aesar	42	75	56.00* for 250 g (Product Code: 39724, Alfa Aesar, USA) As per the price available in the Alfa Aesar by Thermo Fisher Scientific online shopping site (www.alfaaesar.com)	$ 0.224 or Rs. 16.57 per g
Vulcan XC-72R	Cabot Corporation	30	254	50.00** for 50 g (Product Code: 590106-1) As per the price available in the online shopping website of "Fuel Cell Store" (www.fuelcellstores.com)	$ 1.00 or Rs. 73.97 per g

* The cost of 250 g acetylene black is $ 56.00 (Rs. 4142.35); 1 $ = Rs. 73.97

** The cost of 50 g Vulcan XC-72R is $ 50.00 (Rs. 3698.53); 1 $ = Rs.73.97

3.2 Experimental setup

3.2.1 Half cell studies

The electrochemical analyses and measurements of anode electrocatalysts were performed using a Potentiostat/Galvanostat (Autolab Model PGSTAT 204, Netherlands). The Potentiostat/Galvanostat (PGSTAT) is an electronic device consisting of three electrodes cell configuration. The fabricated anode electrode was the working electrode, and silver chloride electrode Ag/AgCl in saturated KCl and a long platinum wire were used as the reference electrode and the counter electrode, respectively (Fig 3.1). The tip of a long strip of carbon paper was coated with Nafion$^®$ impregnated electrocatalyst ink to fabricate the working electrode.
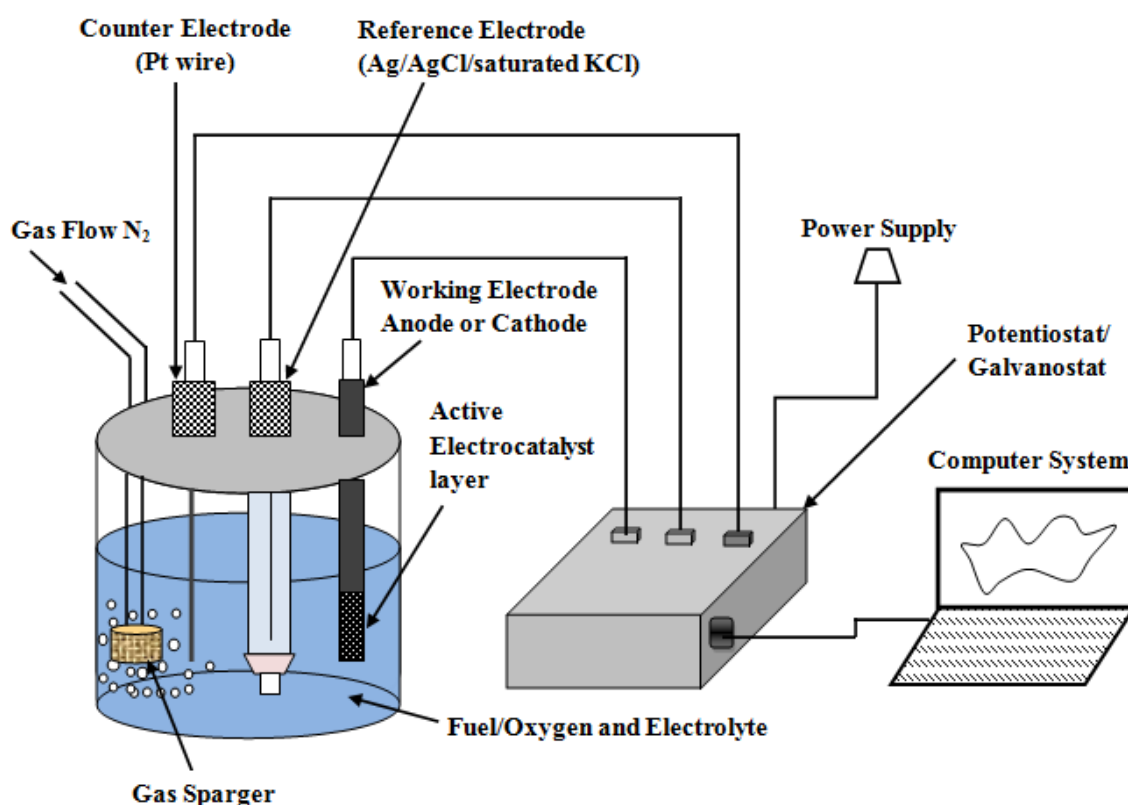

Figure 3.1 Schematic of the three-electrode half-cell experimental set-up to study single electrode performance.

The rest of the strip was connected to the PGSTAT using a standard connecting wire. The active part of the working electrode was immersed in a solution mixed with ethanol fuel of various concentrations and electrolyte ($HClO_4$). To maintain the inert atmosphere, high purity nitrogen gas was bubbled through the solution at a flow rate of 10 mL/min using a silicone tube from an N_2 cylinder for 30 min. The terminals of reference and counter electrodes were also attached to the PGSTAT for electrochemical measurements. The PGSTAT was linked to a Desktop computer that recorded all current-voltage data and the voltammograms were generated using NOVA software (Pramanik and Basu, 2011).

3.2.2 Direct ethanol fuel cell (DEFC)

A commercial fuel cell set-up was used to evaluate the performance of synthesized anode electrocatalysts in single cell DEFC tests (Fig 3.2). The laboratory prepared membrane electrode assembly (MEA) was clamped and placed between two flow channels of cross-section. The flow channels were machined on the graphite blocks of 2.5 cm $\times$ 2.5 cm. Both the flow channels were consisting of serpentine flow channels for ethanol and air flow systems as shown in Fig (3.3). The PTFE tape was used for insulation and leakage prevention on both sides of the MEA. The gold plated copper plates placed next to the graphite block/flow channels were used as current collectors. Two electric heaters were mounted between the current collector and end plates for heating purposes. The cell was then assembled by tightening bolts with uniform torque at the four corners of the end plate of the cell assembly. The DEFC tests were carried out with a constant supply of fuel ethanol at a fixed flow rate to the anode side using a peristaltic pump (Electrolab, India). The humidified oxygen gas fed to the cathode side from the oxygen cylinder. The voltage-current (V-I) data of polarization curves were obtained for each set of experiments by measuring cell voltage at various currents using the DC Electronic Load

Bank (K-PAS, India) at steady-state cell output. The photographic view of the experimental set-up is illustrated in Appendix A (Fig A.1, Page no. 275).
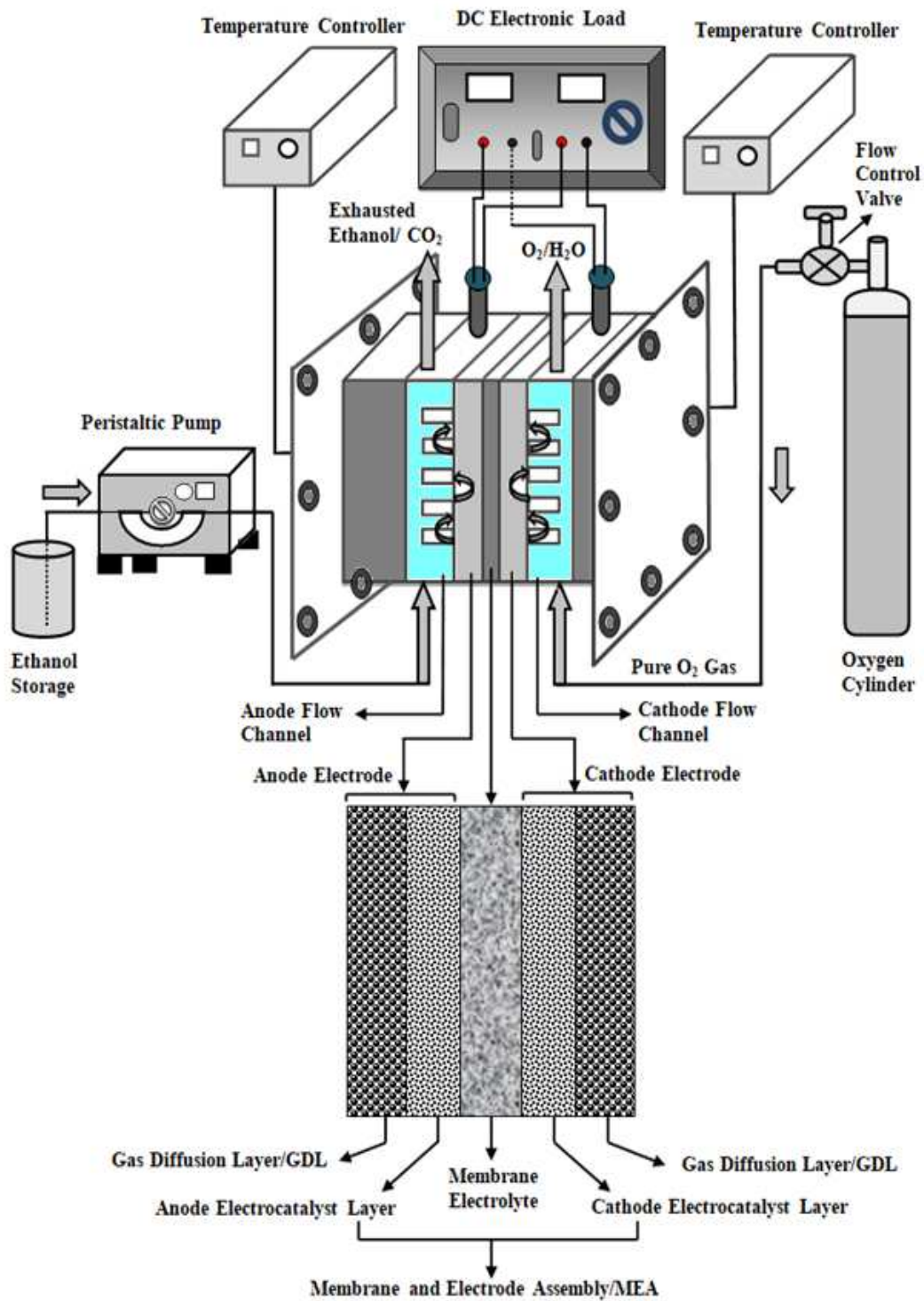

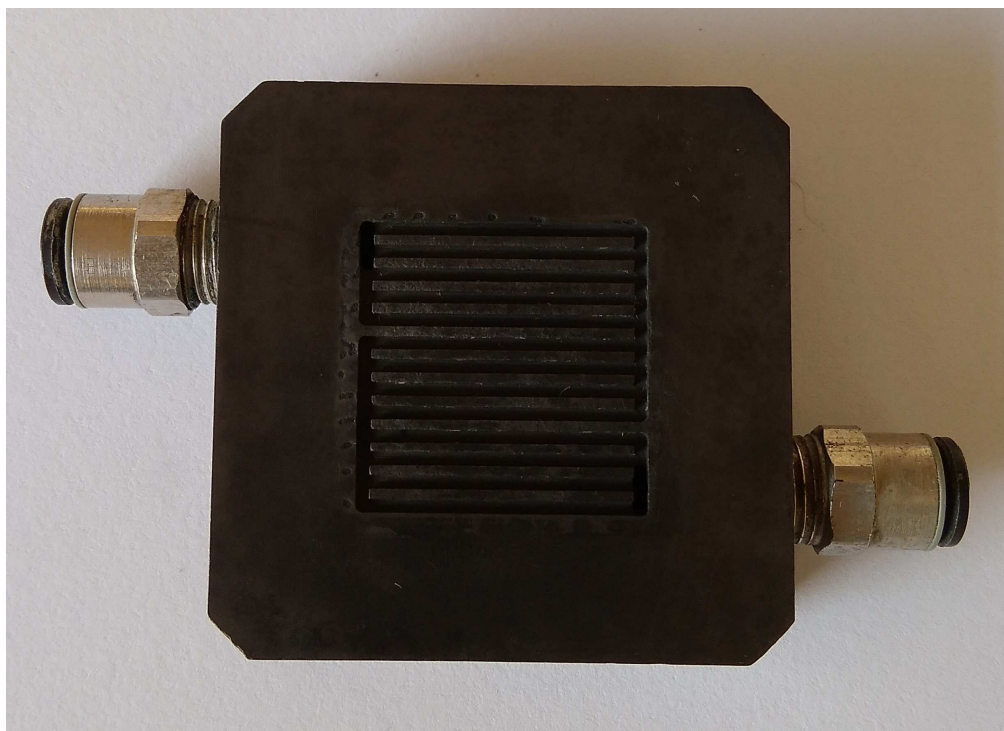**Figure 3.2** Schematic of single direct ethanol fuel cell (DEFC) set-up.

Figure 3.3 Photographic view of the flow channel.

3.3 Methods

3.3.1 Functionalization of support materials

In the present study, pristine acetylene black (C_{PAB}) and pristine multi-walled carbon nanotubes (p-MWCNT) were used as the support material for the synthesized electrocatalysts. Pristine acetylene black (C_{PAB}) was first treated with 60 wt. % HNO_3 acid. The treated carbon sample was then refluxed at a temperature of 140 ℃ for 6 h under vigorous stirring. After cooling, the functionalized acetylene black (C_{AB}) was diluted with distilled water and filtered. To remove any traces of acid present in functionalized acetylene black, the filtered C_{AB} was thoroughly washed with distilled water. The obtained C_{AB} was then dried in a hot air oven at a temperature of 80 ℃ for 8 h

to remove free moisture (Lakshmi et al., 2006). The dry mass of functionalized/treated acetylene black was referred to as C_{AB}.

The pristine multi-walled carbon nanotubes (p-MWCNT) was acid-treated as stated below in order to purify the impurities, increase the dispersion properties and introduce oxygen-containing surface functional groups as nucleation sites, such as carboxylic acid and hydroxyl groups. The p-MWCNT of 0.5 g was initially dissolved in a solution mixture of 8 M HNO_3 and 2 M H_2SO_4, accompanied by ultrasonic blending for 2 h at room temperature of 30 ºC (Li et al., 2003 and Hsu et al., 2008). Then, the obtained mixture was refluxed for 6 h at a temperature of 120 ºC under continuous stirring in a three-necked round bottom flask. To decrease the acidity of the solution, the obtained solution was diluted with distilled water. The diluted solution was then filtered and washed with distilled water until the pH was neutral. Finally, it was dried overnight in a vacuum oven at a temperature of 80 ºC. The dried carbon powder was designated as functionalized multi-walled carbon nanotubes (f-MWCNT).

3.3.2 Electrocatalyst synthesis

The appropriate amount of the metal precursors were used to obtain the prescribed metal composition of bi-metallic and tri-metallic electrocatalysts with nominal metal loading of 40 wt. % on carbon support either C_{AB} or f-MWCNT irrespective of the synthesis methods adopted. The various synthesis methods are adopted in the thesis based on the literature survey are discussed below systematically. The same nominal metal loading of 40 wt. % with Pt to Ru atomic ratio of 1:1 was used for synthesis of bi-metallic Pt-Ru nanoparticles supported on C_{PAB} or C_{AB}, irrespective of the preparation routes adopted.

3.3.2.1 Formic acid reduction method (FAM)

As proposed by Álvarez et al., (2010), the formic acid reduction method (FAM) was adopted for electrocatalyst synthesis. The carbon support functionalized acetylene black (C_{AB}) of 60 mg was suspended in 60 mL (2 mol L^{-1}) formic acid solution using an ultrasonic water bath and the resulted suspension was heated at a temperature of 80 °C. An appropriate amount of metal precursors chloroplatinic acid ($H_2PtCl_6.6H_2O$) for platinum (Pt) and ruthenium chloride ($RuCl_3$) for ruthenium (Ru) were suspended in isopropanol separately and ultrasonicated for 3 h. The precursors solutions were mixed together using a magnetic stirrer and slowly added to the carbon suspension. Then the precursor mixture was followed by another mixing by magnetic stirrer at a temperature of 85 °C for 4 h. The heated suspension was left to cool down to room temperature, and the residue of electrocatalyst was recovered by filtration with Whatman No. 42 filter paper, followed by washing with distilled water until no chloride ions could be detected. The recovered filtered electrocatalyst residue was then dried for 8 h at a temperature of 80 °C in a vacuum oven. The obtained electrocatalysts were named as Pt-Ru (26.35 %: 13.65 % by wt.)/C_{PAB}-FAM or Pt-Ru/C_{PAB}-FAM and Pt-Ru (26.35 %: 13.65 % by wt.)/C_{AB}-FAM or Pt-Ru/C_{AB}-FAM.

3.3.2.2 Polyol reduction method (PLM)

The polyol reduction method (PLM) was also adopted for the electrocatalyst synthesis as proposed by Lee et al., (2010) and Lee et al., (2011). In the polyol reduction process, ethylene glycol was used as a solvent and as a reductive agent for metal precursors. The required amounts of metal precursors i.e., $H_2PtCl_6·6H_2O$ and $RuCl_3$ solutions were added in the ethylene glycol (1 mL EG/1 mg metal) and mixed by an ultrasonic water bath for 1 h. The functionalized acetylene black (C_{AB}) was dispersed separately in diluted ethylene

glycol solution using an ultrasonic water bath for 30 min accompanied by continuous stirring for 1 h to make carbon slurry. The prepared precursor suspension was then added dropwise to the carbon slurry and the pH of the mixture was adjusted approximately to 12-13. The mixture was then refluxed at a temperature of 170 ºC for 4 h to reduce the metal electrocatalyst Pt-Ru/C_{AB} adequately (Guo et al., 2007). In order to eliminate the organic by-products and dissolved oxygen, high purity nitrogen (N_2) gas was purged through the reaction mixture. The reduced electrocatalyst mixture was then cooled to room temperature using a cold water bath. The pH of the mixture was measured and adjusted again to 1.5-2 by adding a few drops of 2 M H_2SO_4 solution. The resulting mixture was heated to a temperature of 70 °C for 3 h under intense stirring to promote the attachment of Pt-Ru colloidal nanoparticles to the carbon support surface. The synthesized electrocatalyst suspension was filtered and washed with hot distilled water until the pH of the filtered water was neutral. The recovered electrocatalyst residue was dried in a vacuum oven at a temperature of 80 °C for 8 h. The obtained electrocatalysts were named as Pt-Ru (26.35 %: 13.65 % by wt.)/C_{PAB}-PLM or Pt-Ru/C_{PAB}-PLM for the synthesized electrocatalyst supported on pristine acetylene black carbon (C_{PAB}). While it was designated as Pt-Ru (26.35 %: 13.65 % by wt.)/C_{AB}-PLM or Pt-Ru/C_{AB}-PLM for the synthesized electrocatalyst supported on functionalized acetylene black carbon (C_{AB}).

In another preparation, a requisite amount of platinum (Pt)-based metal precursor $H_2PtCl_6 \cdot 6H_2O$ was also used to synthesize Pt supported on functionalized acetylene black C_{AB}, i.e., Pt (40 wt. %)/C_{AB}-PLM to examine the formation of Pt-Ru alloy in the synthesized bi-metallic electrocatalysts.

The modified polyol reduction route with post-treatment of electrocatalyst as proposed by Wang et al., (2011), Lee et al., (2010) and Lee et al., (2011) were also used for the

synthesis of functionalized carbon-supported Pt-Ru to see the enhancement of electrocatalytic activity of the synthesized Pt-Ru/C_{AB} for the electrooxidation of ethanol. The same nominal metal loading with Pt to Ru atomic ratio of 1:1 was used as mentioned earlier. The required amount of metal precursors H_2PtCl_6. $6H_2O$ and $RuCl_3$ were dissolved in aqueous ethylene glycol solution (5 % distilled water by volume) and subjected to ultrasonic dispersion in an ultrasonic water bath for 3 h. The pH of the suspension was increased to 12-13 approximately with dropwise addition of 1 M NaOH solution in ethylene glycol, followed by vigorous stirring for 30 min at room temperature. Subsequently, the suspension mixture was refluxed in a three-necked flask at a temperature of 140 °C for 4 h to ensure the total reduction of the metallic precursors and to form the dark brown color of colloidal PtRu nanoparticles. High purity nitrogen gas was passed through the reaction system to eliminate dissolved oxygen and organic by-products. The required amount of functionalized carbon support was separately dispersed in an aqueous solution of ethylene glycol with ethylene glycol to distilled water ratio of 1:1 by volume. The mixture was ultrasonicated for 3 h and vigorously stirred for 1 h to form homogeneous slurry. The prepared colloidal of Pt-Ru nanoparticles were added drop wise to the dispersed carbon slurry and mixed. After 30 min of vigorous stirring, the pH of the slurry was adjusted to about 2 by adding a few drops of 2 M H_2SO_4 solution. The resulting suspension mixture was heated at a temperature of 80 °C and kept for 6 h under intense stirring to deposit Pt-Ru colloidal nanoparticles on the surface of the carbon support. After the stirring, the black suspension was cooled to room temperature, filtered, and washed thoroughly with hot distilled water. Finally, the cleaned precipitate was dried in a vacuum oven at a temperature of 80 °C for 12 h and uniformly ground into a fine powder with mortar and pestle. The obtained electrocatalyst powder was designated as Pt-Ru/C_{AB}-syn. The obtained Pt-Ru/C_{AB}-syn electrocatalyst was subsequently post-treated in

a tube furnace under three different conditions: (i) at room temperature of 30 ºC for 1 h in high purity hydrogen gas, (ii) at a temperature of 160 ºC for 1 h in high purity hydrogen gas and (iii) at a temperature of 160 °C for 1 h in an air atmosphere (Fig 3.4). The consequent post-treated electrocatalysts were denoted as Pt-Ru/C_{AB}-H$_2$-RT, Pt-Ru/C_{AB}-H$_2$-160, and Pt-Ru/C_{AB}-Air-160 according to the above-defined conditions (i), (ii) and (iii), respectively (Choudhary and Pramanik, 2020a).
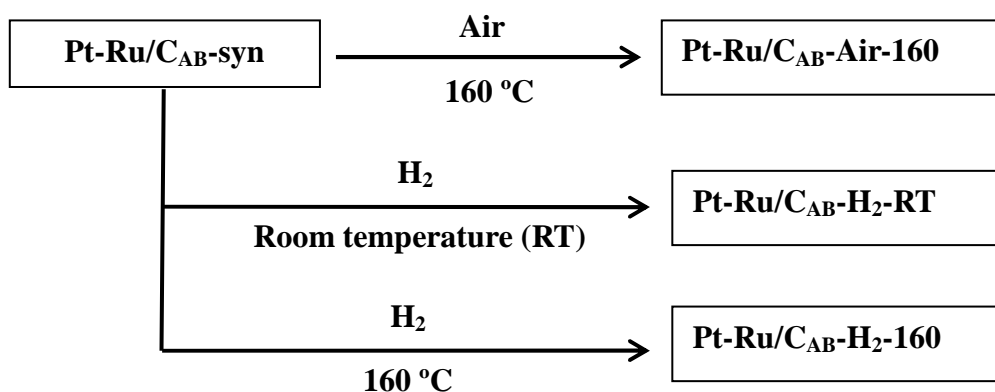

Figure 3.4 Scheme of post-treated conditions of the Pt-Ru/C_{AB}-syn electrocatalyst by modified polyol method.

As it is reported in the literature review (Page no. 30), the tri-metallic electrocatalysts are better than the bi-metallic electrocatalysts for ethanol electrooxidation. Thus, electrocatalysts containing Pt, Ru, and Re supported on functionalized MWCNT (f-MWCNT) with fixed metal loading of 40 wt. % on f-MWCNTs support were also synthesized using the modified polyol reduction method as reported elsewhere (Lee et al., 2011, Choudhary and Pramanik, 2019 and Choudhary and Pramanik, 2020a). Initially, the appropriate stoichiometric amount of metal precursors of $H_2PtCl_6.6H_2O$, $RuCl_3$, and $ReCl_3$ were dispersed in ethylene glycol-water solution (5 vol. % of distilled H_2O) by ultrasonication in an ultrasonic water bath for 3 h at room temperature. The pH of the suspension was modified with 1 M NaOH in ethylene glycol solution in the alkaline range
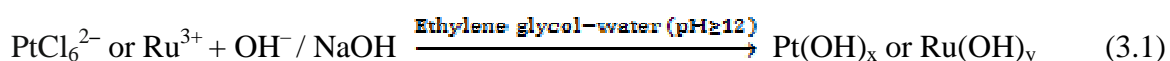
(pH approx. 9-10) and vigorously stirred for 30 minutes at room temperature of 30 °C. The composition of the electrocatalysts was regulated by the variation of the atomic proportion between Pt, Ru and Re metal precursor solution, as indicated below. The resulting mixture was refluxed in a three-necked round bottom flask at a temperature of 140 ℃ under mechanical stirring for 4 h with continuous nitrogen purging to remove the dissolved oxygen and organic by-product. Subsequently, the above-prepared colloid nanoparticles were pipetted drop wise to the ultrasonically-dispersed f-MWCNT suspension, followed by ultrasonication for 30 min. After that, the pH value of the suspension mixture was adjusted to about 2 with addition of 2 M H_2SO_4 aqueous solution and the resulting solution mixture was stirred vigorously at a temperature of 80 ℃ for 6 h. Finally, the obtained electrocatalyst was filtered, washed thoroughly with abundant hot distilled water of 45 ℃ and dried in a vacuum oven at a temperature of 80 ℃ for 12 h. The dried solid nano-composite was eventually ground into a fine powder with mortar and pestle. Table (3.7) summarizes the different types of synthesized bi-metallic and tri-metallic electrocatalysts and their compositions (Choudhary and Pramanik, 2020b).

Table 3.7 Metal compositions of various synthesized bi-metallic and tri-metallic electrocatalysts supported on f-MWCNT.
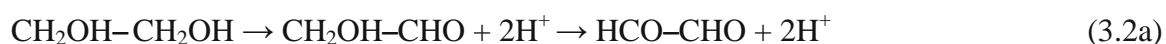
Electrocatalyst	Percentage by wt.				Atomic ratio (Pt:Ru:Re) based on the precursor
	Pt	Ru	Re	f-MWCNT	
Pt-Ru/f-MWCNT	26.35	13.65	---	60	1.0:1.0
Pt-Re/f-MWCNT	20.47	---	19.53	60	1.0:0.0:1.0
Pt-Ru-Re/f-MWCNT	16.17	8.38	15.44	60	1.0:1.0:1.0
Pt-Ru-Re/f-MWCNT	20.04	10.38	9.57	60	1.0:1.0:0.5
Pt-Ru-Re/f-MWCNT	22.76	11.80	5.437	60	1.0:1.0:0.25

3.3.2.2.1 Reaction mechanism of the modified polyol reduction process

Several reaction mechanisms have already been explored in previous studies for the modified polyol reduction (Fievet et al., 1989, Komarneni et al., 2002, Bock et al., 2004 and Yang et al., 2004). In the modified polyol reduction process, Pt and Ru are co-reduced and deposited from their ion salts dissolved in ethylene glycol-water solution on the surface of substrates. In the first step of the modified polyol process, the hydrolysis reaction between metal salt ions and NaOH produces metal hydroxide colloid at high pH (≥ 12) via the following reaction (Equation 3.1) as suggested by Wang et al., (2005).

$$PtCl_6^{2-} \text{ or } Ru^{3+} + OH^- / NaOH \xrightarrow{\text{Ethylene glycol}-\text{water (pH} \geq 12)} Pt(OH)_x \text{ or } Ru(OH)_y \qquad (3.1)$$
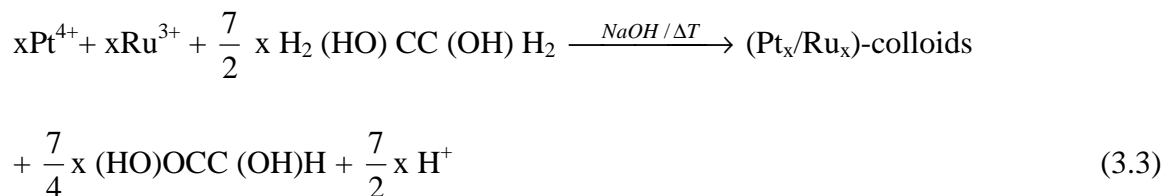
In addition, after receiving electrons from the oxidation of ethylene glycol to glycolic acid, the generated metal hydroxide colloids were reduced as per the reaction mechanism proposed by Bock et al., (2004). Since ethylene glycol is a very weak acid and thus, it can be thermally oxidized to aldehydes at a temperature of 140 °C via the interaction with OH^- groups of ethylene glycol with Pt and Ru ion sites.

$$CH_2OH-CH_2OH \rightarrow CH_2OH-CHO + 2H^+ \rightarrow HCO-CHO + 2H^+ \qquad (3.2a)$$

$$CH_2OH-CHO \rightarrow CH_2OH-COOH \qquad (3.2b)$$

$$CH_2OH-COOH \text{ or } HCO-CHO \rightarrow COOH-COOH \qquad (3.2c)$$

$$COOH-COOH \rightarrow 2CO_2 + 2H^+ \text{ or carbonate} \qquad (3.2d)$$

In the reaction mechanism (Equation 3.2a), the unstable aldehydes formed are not very stable and thus, undergo further oxidation to form glycolic acid (Equation 3.2b) and oxalic acid (Equation 3.2c) respectively. In addition, these two carboxylic acids in alkaline media may be oxidized into CO_2 or carbonate (Equation 3.2d). The electrons donated by oxidation reactions result in the reduction of the Pt and Ru metal ions to form

Pt-Ru metal colloids via Equation (3.3). Glycolic acid in the form of glycolate anion of

deprotonated state is present in the alkaline medium, acts as a stabilizer by forming

chelate-type complexes via its carboxyl groups (Bock et al., 2004 and Oh et al., 2007).

$$xPt^{4+} + xRu^{3+} + \frac{7}{2} x\ H_2\ (HO)\ CC\ (OH)\ H_2 \xrightarrow{\ NaOH\ /\ \Delta T\ } (Pt_x/Ru_x)\text{-colloids}$$

$$+ \frac{7}{4} x\ (HO)OCC\ (OH)H + \frac{7}{2} x\ H^+ \tag{3.3}$$

The stabilizing effect of the concentration of glycolate anion depends on the pH of the

reaction mixture. The concentration of glycolate anion is predicted to remain stable at a

higher pH (pH $\geq$ 6). The stabilizing effect of glycolate anion helps to regulate the particle

size of the Pt-Ru metal colloids. However, due to higher proton and Cl$^-$ ion

concentrations, the stabilizing effect of glycolate anion is destroyed when the pH value is

reduced to about 2. The glycolate anion is substituted by glycolic acid (protonated state)

which is a weak stabilizer and, as a result, reduced Pt-Ru metal particles are accumulated

at active sites of the carbon support.

3.3.3 Physicochemical characterization of support and electrocatalyst

3.3.3.1 Fourier transform infrared spectroscopy (FTIR)

In order to characterize the particular chemical groups in the support materials, Fourier

transform infrared spectroscopy (FTIR) was used. FTIR spectroscopy is a non-destructive

technique for characterizing materials based on the fact that molecules absorb particular

frequencies according to their structures. The FTIR measurements were carried out using

the Nicholet iS5 (Thermo Electron Scientific, USA) spectrometer in the transmission

mode at room temperature to analyze the surface functional groups in a region between

500 cm^{-1} and 4000 cm^{-1} wavenumber. Before the tests, approximately 1 mg of the finely

ground sample was mixed with 100 mg potassium bromide (KBr) powder and the mixture was compressed into a pellet.

3.3.3.2 pH-meter

The pH of the pristine and functionalized acetylene black carbon support material (C_{PAB} and C_{AB}) were recorded using the pH-meter CL54+ (TOSHCON, India). The sample slurry was prepared by ultrasonic dispersion of 1 g of acetylene black carbon in 30 ml distilled water followed by mixing with the help of magnetic stirrer to prepare homogeneous slurry. The pH of the suspension was recorded in a steady state at room temperature of 30 °C.

3.3.3.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) is an effective tool for studying the crystalline structure and size of materials. There are four main components in an XRD system, such as the X-ray source, specimen stage, optics receiving, and detector for X-rays (Sharma et al., 2012). The X-ray diffractometer uses an X-ray beam of a single wavelength for material analysis. The incident angle of the X-ray beam is continuously varied and the diffraction intensity spectrum versus the angle between the incident and the diffraction beam is recorded (Leng, 2009). The XRD patterns were obtained at room temperature on a Rigaku Ultima IV, Germany diffractometer equipped with nickel filtered Cu K_α X-ray source (λ = 0.154187 nm), operating at 40 kV and 15 mA. The diffraction patterns were recorded at a scanning rate of 5° min^{-1} for every 2θ angle in the range of $10 \leq 2\theta \leq 90$ with a step size of 0.02°. The average crystallite size was calculated using the Debye-Scherrer's equation (Equation 3.4) based on the Pt (220) peak broadening of XRD diffractogram (Antolini

and Cardellini, 2001, Antolini et al., 2001, Yang et al., 2012 and Choudhary and Pramanik, 2019).

$$d_c = \frac{\kappa \times \lambda}{\beta \cos \theta} \qquad (3.4)$$

where d_c is the average crystallite size, κ is a geometric factor (0.9 for spherical crystallite), θ is the diffraction angle, β is the width of the peak (in radians) at its half-height, and λ is the wavelength of X-rays used (1.54056 Å for Cu-K$_{\alpha 1}$ radiation).

The lattice parameter value of electrocatalyst was determined from Bragg's law (Equation 3.5) (Velazquez-Palenzuela et al., 2010).

$$n\lambda = 2 d_{hkl} \sin \theta \qquad (3.5)$$

where n represents the order of diffraction (generally $n = 1$, taken most of the cases), d_{hkl} is the interplanar distance between two planes of Miller index (*hkl*), and all other symbols have the same meaning as in Equation (3.4). For the crystalline cubic symmetry, d_{hkl} is a function of Miller indices (*hkl*) and lattice parameter (a), which is expressed as follows:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (3.6)$$

3.3.3.4 Field-emission scanning electron microscopy (FESEM)

The surface morphology and texture of the electrocatalysts were observed by FESEM using a Nova Nano SEM 450 (FEI Company, USA). The image is generated using electrons, instead of light in high resolution scanning electron microscopy. The emitted electrons pass through a series of magnetic lenses for focusing the electron beam on a

small spot. A detector detects the number of secondary electrons emitted and the image is formed on the screen based on the number of electrons (Zhou et al., 2006). The electrocatalyst samples were coated with the conducting layer of gold plating before the FE-SEM analysis. The bulk composition of the electrocatalysts was analyzed using an energy dispersive X-ray (EDX) analyzer integrated into the FESEM instrument and Octane Plus SDD detector (EDAX Inc., USA) was used to analyze the elemental composition.

3.3.3.5 Transmission electron microscopy (TEM)

The morphology, microstructure, particle size distribution and mean particle size of the electrocatalysts were evaluated from TEM images obtained on a Tecnai G2 20 Twin (FEI Company, USA). The samples were prepared by applying a drop of ultrasonically dispersed electrocatalyst suspension in ethanol onto a holey carbon-coated copper TEM grid of 200 mesh size using a micropipette and dried in a vacuum oven at a temperature of 60 ºC for 3 h. Particle size distribution histogram was calculated by measuring the diameter of approximately 150 nanoparticles for each electrocatalyst sample in the corresponding TEM images using Image J software. The average particle size (d_p) was determined using the following Equation (3.7):

$$d_p = \sum \frac{(i)n_i d_i}{n} \tag{3.7}$$

where n_i is the frequency of occurrence of the electrocatalyst nanoparticles with diameter of size d_i and n is the total number of counted electrocatalyst nanoparticles.

3.3.3.6 X-ray photoelectron spectroscopy (XPS)

The XPS measurements were on a spectrometer (AMICUS, Shimadzu Group Company, Japan) equipped with a monochromatic Mg-Kα (1,253.6 eV) X-ray radiation source. The sample was pre-treated in a high-pressure cell catalytic chamber which was connected via a gate valve to the analysis chamber. It was cooled to room temperature in the flowing nitrogen after pre-treatment. The high-pressure cell was then evacuated and the sample was moved in a high vacuum analysis chamber where the XP spectra were generated. The binding energies were calibrated with respect to the C (1s) peak value of 284.6 eV with a precision of ± 0.2 eV. The XPS spectra were curve fitted by spin-orbit splitting with a Shirley background function and Gaussian-Lorentzian function using the XPS PEAK 4.1 software (Beyhan et al., 2013). Initially, the baseline, with Shirley, Linear and Tougaard type were tried for the deconvolution of peaks. The baseline with Shirley background function was statistically found more significant rather than other methods. Hence, Shirley type background function is used as baselines set for XPS analyses (Lee et al., 2011, Beyhan et al., 2013, Corradini et al., 2015, Jacob et al., 2015 and Choudhary and Pramanik, 2019). The relative surface concentration of different oxidation states of Pt was determined from the corresponding deconvoluted peak areas divided by the total XPS signal area obtained from the experimental XPS core-level regions of Pt 4f.

3.3.4 Preparation of anode, cathode and membrane electrode assembly (MEA)

In order to achieve maximum cell output in terms of current density and cell voltage, the anode and cathode electrodes should be properly manufactured. The direct ethanol fuel cell (DEFC) electrodes are generally porous in nature to ensure the diffusion of liquid fuel ethanol and oxidant oxygen through the gas diffusion layer (GDL) to the active anode and cathode regions, respectively. The electrocatalysts tested on the anode side were

synthesized electrocatalysts Pt-Ru/C$_{PAB}$-PLM, Pt-Ru/C$_{PAB}$-FAM, Pt-Ru/C$_{AB}$-PLM, Pt-Ru/C$_{AB}$-FAM, Pt-Ru/C$_{AB}$-syn, Pt-Ru/C$_{AB}$-H$_2$-RT, Pt-Ru/C$_{AB}$-H$_2$-160, Pt-Ru/C$_{AB}$-Air-160, Pt-Ru (1:1)/f-MWCNT, Pt-Re (1:1)/f-MWCNT, Pt-Ru-Re (1:1:1)/f-MWCNT, Pt-Ru-Re (1:1:0.5)/f-MWCNT, Pt-Ru-Re (1:1:0.25)/f-MWCNT and commercial Pt-Ru/C (30 % : 15 % by wt). The complete manufacture of highly porous electrodes is a two-step process. Firstly, the carbon slurry was prepared by dispersing high surface area acetylene carbon black (75 m^2/g) of loading 1 mg/cm^2 in a mixture of isopropanol and Nafion$^{®}$ dispersion using an ultrasonic water bath for 30 min. The prepared carbon slurry was then uniformly coated onto the carbon paper/GDL to form a thin microporous carbon layer using a brush and then dried in an oven at a temperature of 80 °C for 1 h. The carbon-coated GDL was used as a substrate for painting electrocatalyst ink which forms a thin layer of an active electrocatalyst zone after drying. The carbon-coated GDL and the electrocatalyst layer together are called the electrode (Fig 3.5).
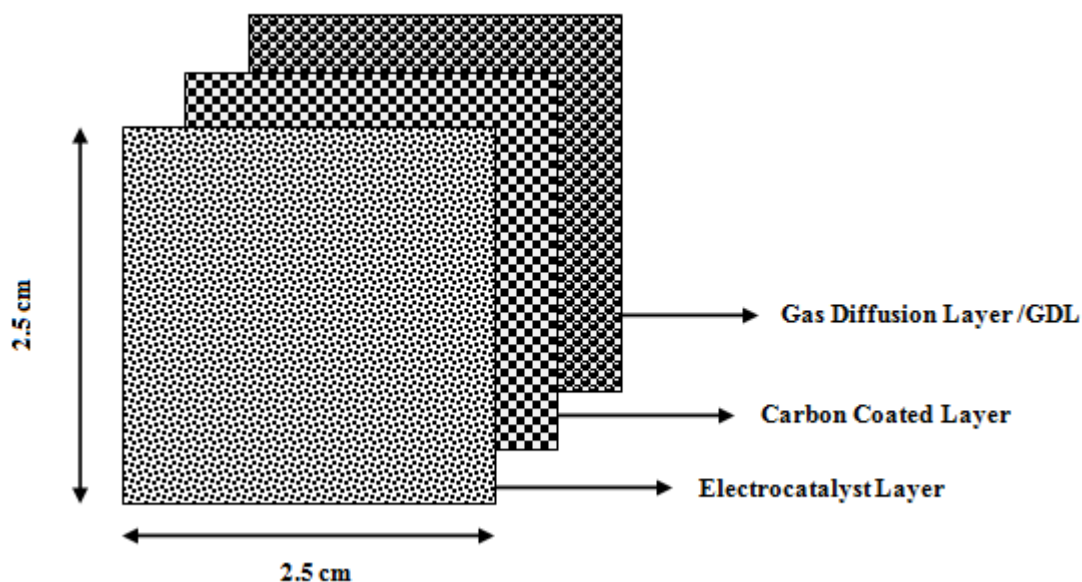

Figure 3.5 Three layers composite of the fabricated electrode.

The manufacturings of anode and cathode electrodes are same except the electrocatalyst used. The anode electrocatalysts were synthesized bi-metallic and tri-metallic alloy materials as discussed earlier (Page no. 93-94). Whereas, the cathode electrocatalyst was commercial Pt/C$_{HiSPEC}$ (40 wt. %) (Page no. 76).

The homogeneous electrocatalyst ink was made by ultrasonic mixing the appropriate amount of electrocatalyst powder, Nafion$^{®}$ ionomer dispersion and isopropanol with a few drops of PTFE dispersion using an ultrasonic water bath at room temperature of 30 ℃ for 30 min. Then, the electrocatalyst ink was then uniformly spread onto a porous carbon paper/GDL using a thin paintbrush, followed by drying in an air oven at a temperature of 80 °C for 1 h. Finally, the dried electrodes were sintered in a vacuum oven at a temperature of 300 °C for 3 h to obtain the porous structure of the anode. This increases the active surface of the electrode with improved mass transfer from the bulk to the active electrocatalyst layer. The cathode was fabricated using the commercial Pt/C$_{HiSPEC}$ (40 wt. %). The active surface area of the GDL i.e., anode and cathode electrodes were of the same dimension 2.5 cm × 2.5 cm (6.25 cm^2). The membrane electrode assembly (MEA) was manufactured by holding the commercial Nafion$^{®}$ 117 membrane/electrolyte in between the sintered anode and the cathode, followed by clamping the assembly together without hot pressing (Nikolić et al., 2011, Zhiani et al., 2011 and Higa et al., 2012) to use it in a single DEFC and evaluate the performance of synthesized electrocatalysts (Fig 3.6).
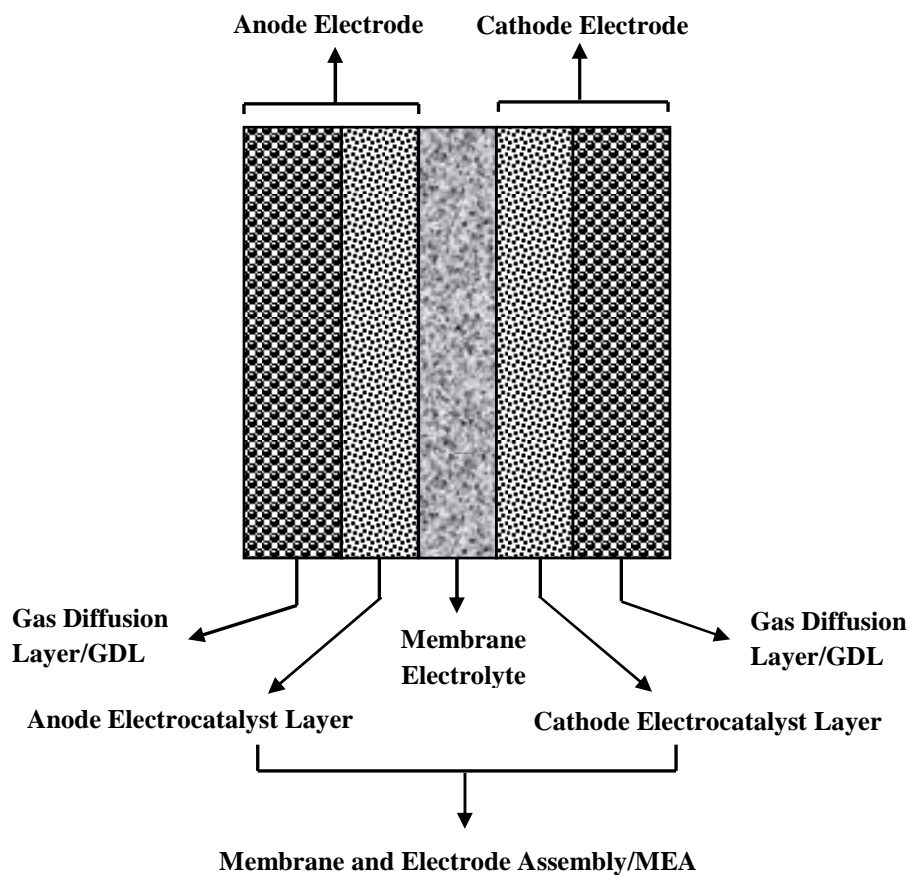
Figure 3.6 Schematic of the clamped MEA.

3.3.5 Electrochemical measurements in half cell

The electrochemical activity of the electrocatalysts towards ethanol electrooxidation was investigated via cyclic voltammetry (CV) and chronoamperometry (CA) tests using a three-electrode cell configuration as shown in Fig (3.1) (Page no. 78). The carbon paper/GDL coated with Nafion® impregnated electrocatalyst ink was used as the working electrode. The electrocatalyst ink was made by mixing 2 mg of electrocatalyst powder in 5 µL Nafion® (5 wt. %) solution and isopropanol (100 µL), which was dispersed in an ultrasonic water bath for 30 min at room temperature to obtain well-dispersed ink. The dispersed ink was deposited on the tip of 0.25 cm² area of a long strip of carbon paper on

a single side (Fig 3.7) and then dried in a vacuum oven at a temperature of 80 ℃ for 1 h.

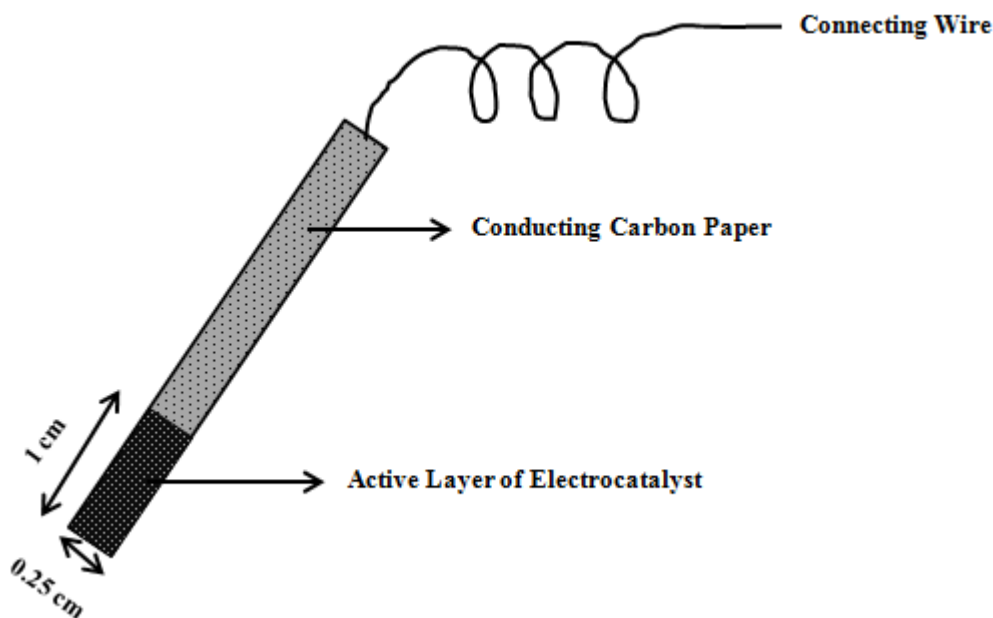The dried electrode was sintered at a temperature of 300 °C for 3 h.

Figure 3.7 Working electrode for electrochemical characterization.

The electrochemical measurements of the developed electrodes were conducted in an acidic solution containing 0.5 M $HClO_4$ mixed with various molar ratios of ethanol. The electrochemical studies were conducted in the voltage range of -0.5 V to 1.0 V at a scan rate of 50 mV/s. To determine the electrocatalytic activity of electrocatalyst for ethanol, cyclic voltammograms (CVs) were carried out in a solution of 0.5 M $HClO_4$ + 1 M or 2 M ethanol between applied voltage 0.0 V and 1.0 V until a stationary response was obtained. The chronoamperometry experiments were recorded to evaluate the stabilities of the electrocatalysts in the same solution for 900 s. Before each experiment, the electrolyte solution was purged with high purity nitrogen to remove the dissolved oxygen molecules from the test solution which could inhibit the electrooxidation of ethanol fuel.

3.3.6 DEFC study

The fuel cell experiments were conducted in a commercial single cell set-up with a geometric active electrode area of 6.25 cm² to generate voltage-current characteristics. The fabricated anode electrodes with various types of synthesized electrocatalysts were tested at different cell conditions. The cathode was fabricated using commercial Pt/C$_{HiSPEC}$ (40 wt. %) electrocatalyst in all experiments. The different aqueous concentrations of ethanol fuel i.e., 0.5 M, 1 M, 2 M, and 3 M were fed into the anode using a peristaltic pump (Electrolab, India) at a set flow rate of 1.2 ml/min. The humidified oxygen of 80 % relative humidity was delivered to the cathode side from the cylinder at a flow rate of 60 ml/min. Before the experiments, the MEAs were fully hydrated by circulating distilled water through the anode and cathode compartments at a temperature range of 30 ºC-80 ºC for 4 h using a peristaltic pump. After that, the cell was activated by passing a certain concentration of ethanol for 2 h to ensure that the anode electrocatalyst layer is surrounded by fuel and electrolyte molecules. The cell polarization data were recorded by measuring the cell potential for each steady-state current data using a DC electronic load (K-PAS Instronic Engineers India Pvt. Ltd.). All the DEFC experiments were carried out at a temperature range of 30 °C-80 °C and 1 bar absolute pressure for both side anode and cathode, respectively.

3.3.7 Stability test of DEFC

The stability tests of DEFC were conducted for both the best bi-metallic and tri-metallic electrocatalysts depending on their performance. The time for evaluation was maintained 15 h under a constant load at a temperature of 30 ºC using optimum DEFC conditions. The operating cell voltage was recorded at an interval of 1 h.