CHAPTER 3

EXPERIMENTAL

In experimental chapter 3, the materials utilized in the synthesis of electrocatalysts and electrode fabrication for half-cell and single cell are discussed in the section 3.1 Materials. The electrocatalyst synthesizing process is discussed in the next section 3.2 under this section 3.2, discusses the precise method used to synthesize the Pt-M/C_{AB} electrocatalysts and followed by electrocatalyst physical characterization, electrochemical characterization, experimental setup are presented systematically in section 3.3, 3.4 and 3.5, respectively.

3.1 Materials

The main reaction process for the synthesis of Pt-M/C_{AB} electrocatalyst was performed in a glass container covered with polytetrafluoroethylene (PTFE) lid followed by another cover of aluminum foil. The metal precursors for Pt and Co were platinum (II) acetylacetonate (Alfa Aesar, USA) and cobalt (III) acetylacetonate (Alfa Aesar, USA), respectively. The acetylene black carbon (C_{AB}) (Alfa Aesar, USA) with a high active surface area of 75 m^2/g was used as a carbon support material to synthesize Pt-Co/C_{AB}. The carbon support C_{AB} also improves the electronic conductivity of the synthesized electrocatalyst. The dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), ethylene glycol (EG) and water (W) were used as mother solvent for the synthesis of three different types of Pt-M/C_{AB}-X (where M = Co and Ni and X are various types of solvents like DMSO, DMF, EG, and W) electrocatalysts. The Pt-Co bimetallic electrocatalysts were designated as Pt-Co/C_{AB}-DMSO for the solvent dimethyl sulfoxide, Pt-Co/C_{AB}-DMF for dimethylformamide, Pt-Co/C_{AB}-EG for ethylene glycol and Pt-Co/C_{AB}-W for water was used as a solvent. Similarly Pt-Ni

electrocatalyst were designated as Pt-Co/C_{AB}-DMSO, Pt-Co/C_{AB}-DMF, Pt-Co/C_{AB}-EG and Pt-Co/C_{AB}-W. The properties of different solvents DMSO, distilled water, EG and DMF are given in Table 3.1 - 3.4, respectively. Highly conducting and porous Tory carbon paper TGH-H-60 (Alfa Aesar, USA) was used as a substrate/gas diffusion layer (GDL) to paint the electrocatalyst ink for the manufacturing of electrodes. The electrode was fabricated with a blend of Nafion® (5 wt. %, Alfa Aesar, USA) and PTFE (60 % by wt., Sigma Aldrich, USA) which act as a binder for electrocatalyst and it also helps to fix electrocatalyst ink on the surface of carbon paper/GDL. The electrolyte $HClO_4$ (Fisher Scientific, India) was used for cyclic voltammetry (CV) analysis in a half-cell configuration. The oxidant pure oxygen from storage/cylinder was used for oxygen reduction reaction study in cyclic voltammetry and single cell also. The inert atmosphere for CV analysis was maintained by purging nitrogen from the cylinder. The properties of Nafion® dispersion, PTFE solution, Toray carbon paper and fuel hydrogen are given in Table 3.5-3.8, respectively.

Table 3.1 Properties of dimethyl sulfoxide (SDFCL, India).

Sr. No.	Properties	Value
1	Boiling point (°C)	189
2	Freezing point (°C)	18.54
3	Density at 25 °C (g/ml)	1.0954
4	Dielectric constant at 25 °C	46.68
5	Vapor pressure (Pa)	10412
6	Viscosity (cP)	0.0310
7	Flash point (°C)	95

Table 3.2 Properties of distilled water (lab made).

Sr. No.	Properties	Value
1	Boiling point (ºC)	100
2	Freezing point (ºC)	0
3	Density at 25 ºC (g/ml)	1
4	Dielectric constant at 20 ºC	78.2
5	Vapor pressure (Pa)	101325
6	Viscosity (cP)	0.890

Table 3.3 Properties of ethylene glycol (Alfa Aesar, India).

Sr. No.	Properties	Value
1	Boiling point (ºC)	197.3
2	Freezing point (ºC)	-8.9
3	Density at 25 ºC (g/ml)	1.113
4	Dielectric constant at 20 ºC	37
5	Vapor pressure (Pa)	44583
6	Viscosity (cP)	16.1
7	Flash point (ºC)	111

Table 3.4 Properties of dimethylformamide (Alfa Aesar, India)

Sr. No.	Properties	Value
1	Boiling point (ºC)	153
2	Freezing point (ºC)	-60.4
3	Density at 25 ºC (g/ml)	0.948
4	Dielectric constant at 25 ºC	36.71
5	Vapor pressure (Pa)	516
6	Viscosity (cP)	0.802
7	Flash point (ºC)	58

Table 3.5 Properties of dimethylformamide (Alfa Aesar, India)

Sr. No.	Properties	Value
1	Boiling point (ºC)	153
2	Freezing point (ºC)	– 60.4
3	Density at 25 ºC (g/ml)	0.948
4	Dielectric constant at 25 ºC	36.71
5	Vapor pressure (Pa)	516
6	Viscosity (cP)	0.802
7	Flash point (ºC)	58

Table 3.6 Composition and properties of Nafion® solution (Alfa Aesar, USA).

Sr. No.	Nafion® solution details	Components/properties of solution	Value
1	Solution compositions	Ethanol (wt. %)	< 4
		Water content (wt. %)	42 – 48
		Solid content (wt. %)	5.0 – 5.4
		VOC Content (wt. %)	47 – 53
		1-propanol (wt. %)	48 – 51
		Mixed ethers and other VOCs (wt. %)	< 1
2	Solution properties	Viscosity (cP; at 25 °C)	10-40
		Available Acid Capacity (meq/g)	> 1
		Specific Gravity	0.92 – 0.94
		Total Acid Capacity (meq/g)	1.03 – 1.12

Table 3.7 Properties of PTFE Dispersion (Sigma Aldrich, USA).

Sr. No.	Properties	Value
1	Concentration	60 wt. % dispersion in H_2O
2	pH	9.5-11
3	Density	1.51 g/mL
4	Particle diameter	0.2 µm
5	Viscosity (C_p, 25 ºC)	25
6	Transition temperature	337 ºC
7	Refractive index	1.350-1.380

Table 3.8 Properties of Toray Carbon paper, TGP-H-60 (Alfa Aesar, USA).

Sr. No.	Properties	Value
1	Porosity (%)	78
2	Surface roughness (µm)	8
3	Thermal conductivity (W/(m.k))	1.7
4	Thickness (mm)	0.19
5	Bulk density (g/cm^3)	0.44
6	Tensile strength (N/cm)	50
7	Electrical resistivity through plane in plane(m Ω cm)	80
8	Flexural strength (MPa)	40
9	Flexural modulus (GPa)	10

Table 3.9 Properties of hydrogen fuel (Alfa Aesar, India).

Sr. No.	Properties	Value
1	Flame temperature (ºC)	2045
2	Melting point (ºC)	-269.20

Sr. No.	Properties	Value
3	Heat of fusion (cal/mole)	28
4	Critical temperature (ºC)	-240
5	Critical pressure (atm)	13
6	Critical density (g/cm^3)	0.0310
7	Auto-ignition temperature in air (ºC)	520-750

3.2 Electrocatalyst synthesis

3.2.1 Synthesis of Pt-Co/C_{AB} cathode electrocatalyst

The solvothermal synthesis method was carried out in a PTFE-covered glass container to synthesize four different types of Pt-Co/C_{AB} cathode electrocatalyst using four solvents one after another viz Pt-Co/C_{AB}-DMSO, Pt-Co/C_{AB}-DMF, Pt-Co/C_{AB}-EG and Pt-Co/C_{AB}-W. The metal composition in the Pt-Co/C_{AB} electrocatalyst were varied i.e., Pt to Co atomic ratio of 3:1, 1:1, 1:3 electrocatalysts with total metal loading of 20 wt. % on 80 wt. % acetylene carbon black (C_{AB}) (S_{BTE} 75 m^2/mg, Alfa Aesar, USA) respectively. The adequate amount of metal precursors of platinum (II) acetylacetonate (98% metal basis, Alfa Aesar, USA) and cobalt (III) acetylacetonate (99% metal basis, Alfa Aesar, USA) were mixed in 12 mL of DMSO (99.9%) or DMF (99.9%) or EG (99.9%) or water (W) solvent to obtain a reaction mixture containing, platinum (II) acetylacetonate of 30 mM and 10 mM cobalt (III) acetylacetonate, respectively for each type of electrocatalyst preparation (Singh and Pramanik 2019). Each prepared reaction mixture was heated at its boiling point for 4 hr keeping the PTFE-covered glass container in an autoclave reactor (Carpenter et al., 2012 and Zhang et al., 2003). After continuous heating of the reaction mixture, the glass container was taken out from the heating oven and kept at room temperature for cooling. The glossy metal alloy of Pt and Co was found to be deposited on the wall of the glass container

and thus, the metal alloy was immersed in 10 mL of ethyl alcohol (99.9%) followed by mixing with the help of an ultrasonic water bath for 30 minutes. Then in another glass beaker 160 mg of carbon support acetylene black (C_{AB}) was immersed in 15 mL of ethanol and thoroughly mixed using an ultrasonic water bath for 30 min at a room temperature of 30 ºC. The C_{AB} slurry was then added to the mixture solution of a metal alloy of Pt and Co dropwise. These two mixtures were further sonicated for the next 30 min followed by another mixing of the homogeneous solution using a magnetic stirrer for 2 hr at a temperature of 40 ºC. The stirred homogeneous solution was then separated in two phases using centrifugation such that solid electrocatalyst Pt-Co/C_{AB} gets settled at the bottom and the yellowish liquid remains at the top. Undesired supernatant yellowish liquid and byproduct were separated from the synthesized Pt-Co/C_{AB} electrocatalyst using filtration followed by two repeated washing cycles; one by 15 mL of ethanol and another by 20 mL distilled water, respectively (Carpenter et al., 2012; Zhang et al., 2003 and Renaud, 1998). Each cycle began with sonication to disperse the electrocatalyst Pt-Co/C_{AB} in the solvent i.e., ethanol and distilled water then centrifugation for the removal of the supernatant. Finally, filtration was used to isolate the synthesized solid Pt-Co/C_{AB} electrocatalyst from the final wash rather than centrifugation. The separated electrocatalyst was kept in a vacuum oven for drying at a temperature of 80 ºC for 2 hr. Then the dried electrocatalyst was heated at a temperature of 200 ºC for 24 hr to get the final form of sintered electrocatalyst Pt-Co/C_{AB}. The final form of the synthesized electrocatalyst Pt-Co/C_{AB} was then used for physical and electrochemical characterization before the final testing in a single PEMFC using H_2 as fuel O_2 as oxidant.

3.2.2 Synthesis of Pt-Ni/C_{AB} cathode electrocatalyst

To synthesize different atomic ratios i.e., 3:1, 1:1, and 1:3 of Pt-Ni/C_{AB} electrocatalysts, the solvothermal synthesis process was carried out in PTFE-lined glass container to synthesize three

different types of Pt-Ni/C_{AB} cathode electrocatalyst viz Pt-Ni/C_{AB}-DMSO, Pt-Ni/C_{AB}-DMF and Pt-Ni/C_{AB}-EG. In the synthesis reaction to produce each electrocatalyst Pt-Ni(3:1)/C_{AB} or Pt-Ni(1:1)/C_{AB} or Pt-Ni(1:3)/C_{AB} the required amount of dihydrogen hexachloroplatinate (IV) hexahydrate (99.90% metal basis) and Nickel (II) chloride hexahydrate (99.9% metal basis) was dissolved in 12 mL different types of solvent namely DMSO, DMF and EG respectively. Each reaction mixture is heated at its boiling point for 4 hr in a PTFE lined glass container keeping it in autoclave reactor (Demazeau 2010; Carpenter et al., 2012). The reaction mixture was obtained after continuous heating of 4 hr, the glass container was taken out from the heating oven and kept at room temperature for cooling. The precipitated metal alloy Pt and Ni on wall of glass container was mixed with 10 mL of ethyl alcohol and then sonicated in an ultrasonic water bath for 30 minutes. Then in another beaker 15 mL of ethanol dispersed with 160 mg of acetylene carbon black was sonicated for 30 min in a water bath ultrasonicator at a temperature of 30 ºC. The C_{AB} slurry was added to alloy solution mixture of Pt and Ni obtained after sonication. These two blends were mixed together and further sonicated for next 30 minutes to obtain metal alloy slurry (Pt-Ni/C_{AB}). Now, metal alloy slurry stirred using magnetic stirrer at temperature of 40 ºC for two hr. The stirred homogenous solution then separated by centrifugation in two phases, one solid Pt-Ni/C_{AB} at bottom and yellowish liquid at top. Undesired supernatant yellowish liquid and byproduct were separated from the synthesized Pt-Ni/C_{AB} electrocatalyst using filtration followed by two repeated washing cycle; one by 15 mL of ethanol and another by 20 mL distilled water, respectively (Demazeau 2010; Carpenter et al., 2012 and Takahasi et al., 1996). Each cycle began with sonication to disperse the electrocatalyst Pt-Ni/C_{AB} in solvent, ethanol and distilled water then centrifugation and removal of the supernatant. The filtration was used to remove the solid Pt-Ni/C_{AB} electrocatalyst from the final wash rather than centrifugation. The separated electrocatalyst

was dried at a temperature of 80ºC for 2 hr. Then the dried electrocatalyst Pt-Ni/C_{AB} was heated at a temperature of 200 ºC for 24 hr to get the final form of sintered electrocatalyst Pt-Ni/C_{AB}. Finally, sintered Pt-Ni/C_{AB} electrocatalyst sent for physical and electrochemical characterization similar to Pt-Co/C_{AB} electrocatalyst before the testing of the Pt-Ni/C_{AB} electrocatalyst in a single PEMFC.

3.3 Physical characterization of Pt-Co/C_{AB} and Pt-Ni/C_{AB} electrocatalyst

3.3.1 X-ray diffraction (XRD)

The XRD diffractometer (Rigaku Ultima IV, Germany) was used to analyze the crystalline structural properties of the synthesized electrocatalysts using the Cu Kα radiation source (λ = 0.154 nm) with Ni filter at a tube current 15 mA. The electrocatalyst sample of 25 mg was used for XRD test. The XRD spectrum was noted for 2θ of 10º to 90º at a scan rate of 5º min^{-1} with an angular resolution of 0.02º. The crystalline phases were analyzed with the Joint Committee on powder diffraction standards (JCPDS 04-0802). The diffraction peak Pt (111) of XRD diffractometer was used to calculate crystallite size was by the Scherrer's equation (equation 3.1) (Zhang et al., 2003). The Bragg's Law (Equation 3.2) was used to calculate the lattice parameters of synthesized electrocatalyst (Safo and Oezaslan 2017; Takahasi et al., 1996).

$$d_c = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{3.1}$$

$$n\lambda = 2d_{hkl}\ \sin\theta \tag{3.2}$$

Where, d_c is calculated crystallite size, λ is X-ray wave length (0.154 nm), β is the width of the peak (in radius) and θ is angle at peak position, n is order of diffraction, d_{hkl} is interplanar distance between two planes of miller index (hkl). For a crystalline cubic symmetry, d_{hkl} is a function of miller indices (hkl) and lattice parameter (α) which is expressed as following (Equation 3.3).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.3}$$

3.3.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX)

The High resolution scanning electron microscope (HRSEM) instrument (Nova Nano SEM 450, FEI USA) recorded the surface morphology data and texture of electrocatalysts electronically. The Energy-dispersive X-ray (EDX) spectroscopy was used to analyze the elemental composition of existing elements in synthesized electrocatalyst using Octane Plus silicon drift detector (SDD) combined with a high-resolution electron scanning microscope (Nova Nano SEM 450), which was attached with HRSEM (Nova Nano SEM 450). The electrocatalyst samples were crafted with the conducting layer of gold plating before the HRSEM analysis.

3.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) (Tecnai G2 20 Twin, FEI USA) measured the particle size of synthesized electrocatalyst at atomic level. The vacuum tube voltage of TEM was maintained at 200 kV. The histogram was obtained using the Image J program to estimate the mean particle sizes from each 100 nm nanoparticles form TEM images. The mean particle size measured from the TEM image was compared with the mean crystallite size obtained from the Scherrer's equation of the XRD pattern. The samples were prepared by applying a drop of ultrasonically dispersed electrocatalyst suspension in ethanol on to a heavy carbon coated copper TEM grid of 200 mesh size using a micropipette and dried in a vacuum oven at 60 ^{o}C for 3 hr.

3.4 Electrochemical characterization of Pt-Co/C_{AB} and Pt-Ni/C_{AB} electrocatalyst

3.4.1 Fabrication of electrode for oxygen reduction reaction (ORR)

The gas diffusion layer (GDL) was fabricated by coating the electrocatalyst ink on a substrate Tory carbon paper of 0.5 cm^2 (1 cm x 0.5 cm) size, which formed a thin layer of active electrocatalyst. The electrocatalyst coated GDL (Figure 3.1(a)) makes a cathode electrode for the diffusion of oxygen because GDL is porous in nature. The electrocatalytic ink was prepared by dispersing the necessary amount of Pt-Ni/C_{AB}, 1-2 drop Nafion ionomer (5 wt. %), acetylene black carbon (C_{AB}), and 1 drop of PTFE (60 wt. %) dispersion for 20 min using an ultrasonic water bath at room temperature. The prepared electrocatalytic ink was then uniformly spread on the one side of the Tory carbon paper GDL strip using a brush to create a stable porous wet film of cathode electrocatalyst. The electrocatalyst coated cathode electrode was then dried in an oven for 1 hr at a temperature of 80 ^oC. The dried cathode electrode was sintered at a temperature of 200 ^oC for 2 hr to get the final form of the electrode (Figure 3.1(b)) (Pramanik and Basu 2007; Basu et al., 2008; Pramanik et al., 2008; Rathoure and Pramanik 2016).

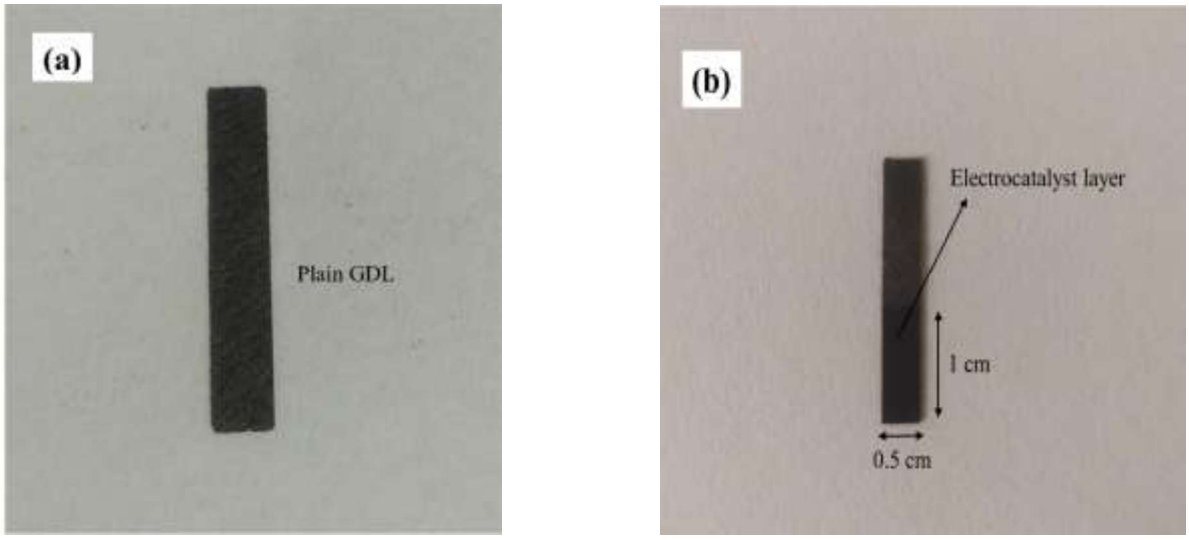

Figure 3.1 Image of (a) gas diffusion layer (GDL), (b) fabricated electrode for half-cell.

3.4.2 Half-cell studies

The cyclic voltammetry (PGSTAT 204, Auto lab Netherlands) experiments were carried out for all the synthesized electrocatalysts in a half-cell having three electrodes assembly at a temperature of 30 ^{o}C. The fabricated cathode electrode i.e., GDL strip/ Toray carbon paper coated with electrocatalyst (section 3.4.1) was used as working electrode. Standard Pt wire was used as counter electrode and Ag/AgCl as reference electrode. The electrocatalyst coated side of the GDL was immersed in the oxygen saturated electrolyte ($HClO_4$) and the other base end of GDL strip was connected to Potentiostat-Galvanostat (PGSTAT) through the external circuit (Figure 3.2). The oxygen saturated electrolyte solution was prepared by purging the oxygen from the cylinder using silicon tube for 1 hr. The potentiostat was linked to a computer that records the current-voltage data, and NOVA 1.10 was used to generate the voltammogram (Pramanik and Basu 2007; Hyun et al., 2013).

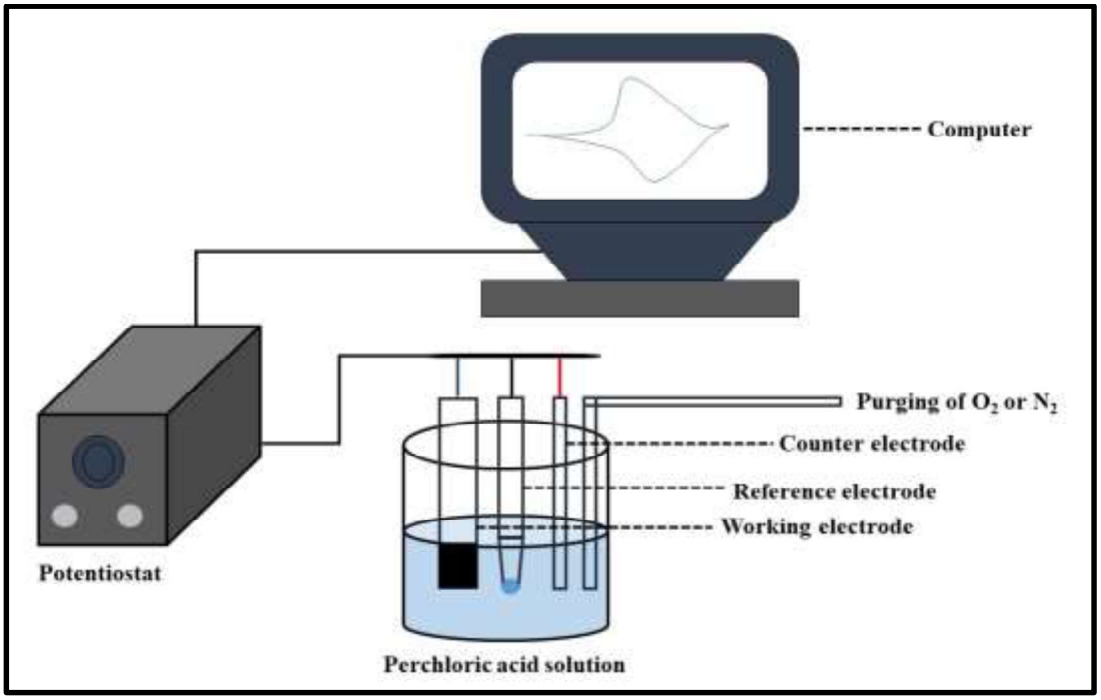

Figure 3.2 Schematic of three electrode cell assembly schematic for conducting CV and EIS experiments using a potentiostat galvanostat (PGSTAT).

3.4.3 Electrochemical impedance spectroscopy (EIS) analysis

The charge transfer resistance of the electrode decides the performance of the cathode electrode. The charge transfer resistance of the cathode was measured by electrochemical impedance spectroscopy. In this measurement, the cathode electrode as manufactured in section 3.4.1 was exposed to oxygen saturated solution of 0.5 M $HClO_4$ at a temperature of 30 ºC. The terminal of the cathode electrode was connected to a Potentiostat-Galvanostat (PGSTAT 204, Autolab Netherland) to get Nyquist-plot using NOVA 1.10 software (Panjiara and Pramanik 2020). The frequency spectrum of the EIS is recoded between 100 kHz and 100 mHz. The diameter of semicircle recorded during the experiment reveals the charging transfer resistance of the electrode in the EIS test. Equivalent circuit (EC) is obtained from the Nyquist plot. The quantitative data like charge transfer resistance, solution resistance and constant phase element is extracted from the Z-view software (version 3.4e, AMETEK, USA).

3.5 Single cell experimental setup and method

The synthesized electrocatalysts were tested in a laboratory fabricated PEMFC single-cell design after systematic electrochemical characterization of the cathode electrocatalysts. The membrane electrode assembly (MEA) Figure 3.3 was placed fixed, between two flow channels of 2.5 cm x 2.5 cm dimension for fuel hydrogen at the anode and oxidant oxygen supply at the cathode, respectively. The PEMFC testing was carried out at 1 atmospheric pressure, operating temperature ranging from 33 ºC to 80 ºC and relative humidity of 80 % (Figure 3.4). The fuel and oxidant flow rate of 50 ml/min and 60 ml/min were maintained at anode and cathode side, respectively.

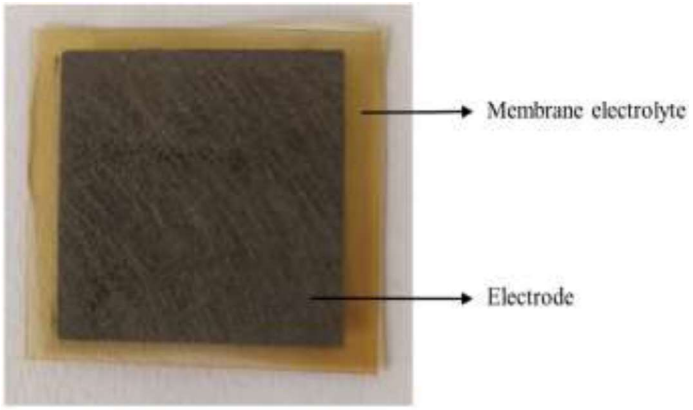

Figure 3.3 Image of membrane electrode assembly (MEA).

The MEA was made by clamping method keeping the membrane electrolyte Nafion®-117 (Alfa Aesar, USA) in between anode and cathode electrode. The anode and cathode electrodes were made of electrocatalyst ink which was prepared in a similar way as that of the electrode manufactured for half-cell analysis described in section 3.4.1 (Page no. 52). All the components for anode and cathode electrodes were the same, except the electrocatalyst. The anode electrocatalyst used was commercial Pt/C (40 wt. % Alfa Aesar, USA). The cathode was made of Pt-M/C_{AB}-DMSO or Pt-M/C_{AB}-DMF or Pt-M/C_{AB}-EG or Pt-M/C_{AB}-W (M= Co, Ni) electrocatalyst synthesized using various types of solvents. Two end plates were attached to the heater which were then placed over the flow channel/current collectors to assemble the entire PEMFC using four bolts positioned at the four corners of the end plates. The electrical heaters were attached to the temperature control system to operate the cell at the desired temperature. The current and voltage data were noted under varying loads using DC electronic load for different types of cathode electrocatalysts, temperature and electrocatalyst loading to obtain the highest power density under those optimized conditions. The photographic view of the PEMFC single cell setup is shown in Appendix A (Figure A1).

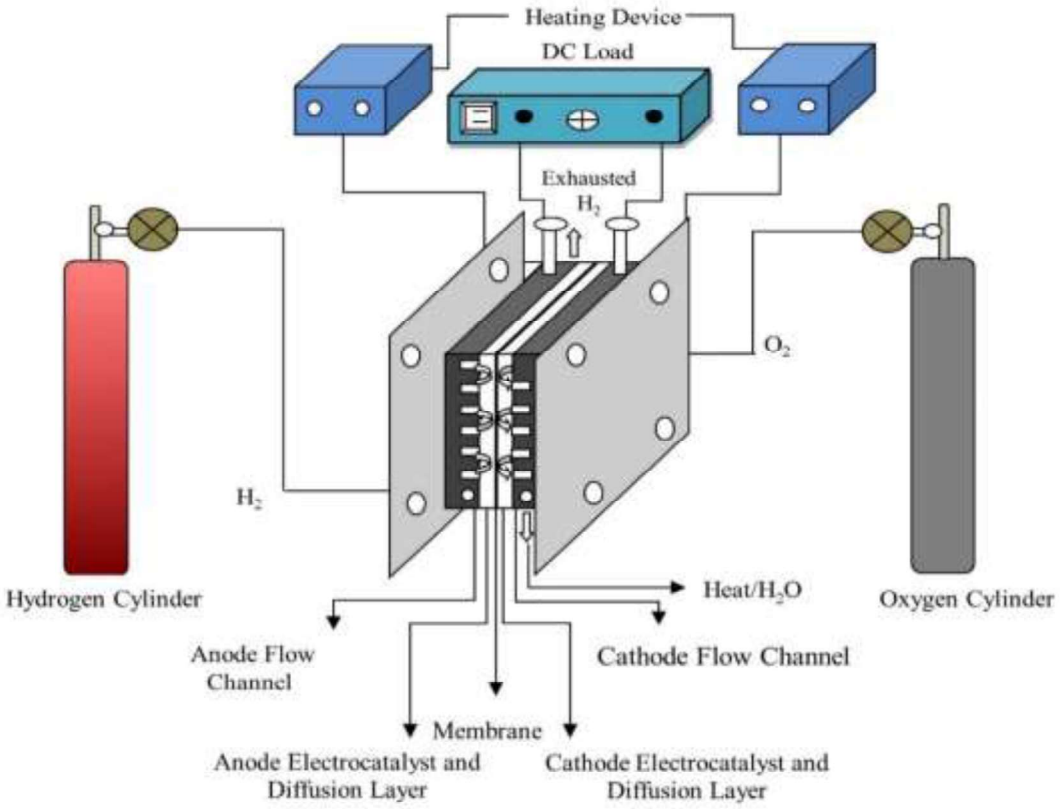

Figure 3.4 Schematic of proton exchange membrane fuel cell experimental set up.

3.6 Stability test

The stability test of the PEMFC was done by taking Pt/C_{HSA} as anode and Pt-Co/C_{AB}-EG as cathode with both having an optimum electrocatalyst loading of 1mg/cm^2. The cell was operated at the maximum power density where optimal starting operational cell voltage of 0.38 V was recorded under load. The cell was operated for 12 hr. The change in optimal voltage at room temperature of 33 ^oC with an interval of 1 hr, data was recorded. Similarly for the Pt-Ni/C_{AB}-EG electrocatalyst the stability test was performed where it replaced Pt-Co/C_{AB}-EG as cathode and at optimal starting operational cell voltage of 0.4 V under load was recorded during startup of the cell. As mentioned earlier, the voltage was recorded up to 12 hr.