

## CHAPTER 3

### EXPERIMENTAL

This chapter includes the materials required for conducting experiments and experimental details related to setup fabrication for half cell and single cell studies along with the manufacturing of different cell components and their characterizations. The important cell components which are considered here are anode, cathode and membrane electrolyte. The anode and cathode manufacturing and their characterization using scanning electron microscopy (SEM) and cyclic voltammetry (CV) are discussed. The characterization techniques of synthesized membrane electrolytes are presented here for their different properties like, water uptake, KOH uptake and ionic conductivity. The synthesized membrane electrolytes were further characterized using high resolution scanning electron microscopy (HR-SEM), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and mechanical testing which are also discussed in this section. The stability of single cell is presented at the end of this chapter.

#### 3.1 Materials

The anode and cathode were prepared using electrocatalysts Pt-Ru (30 % : 15 % by wt.)/ Carbon black (C) (Alfa Aesar, USA) and Pt (40 % by wt.)/ High Surface Area Carbon (C<sub>HSA</sub>) (Alfa Aesar, USA), respectively. Toray Carbon paper (TGP-H-60 Alfa Aesar, USA) was used as substrate or gas diffusion layer (GDL) for applying the electrocatalyst ink using paint brush technique. The typical composition and properties of the Toray carbon paper (TGP-H-60 Alfa Aesar, USA) is given in Table (3.1). Nafion<sup>®</sup> (D-520) and polytetrafluoroethylene (PTFE) (10 wt %) dispersion were used as binder and obtained from Alfa Aesar, USA, and Sigma Aldrich, Germany, respectively. The composition of

Nafion<sup>®</sup> and PTFE dispersion are given in Table (3.2) and Table (3.3), respectively. Methanol and ethanol obtained from Fischer Scientific, India were used as anode fuel. Potassium hydroxide was used in alkaline membrane preparation and as a supporting electrolyte in CV experiments and single cell experiments. The KOH was obtained from Fisher scientific, India. Isopropyl alcohol (AVANTOR<sup>™</sup>, India) was used as diluents.

**Table 3.1** Typical properties of Toray carbon paper (TGP-H-60, Alfa Aesar, USA).

Typical properties	Value
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 mΩ cm
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 3.2** Composition and properties of Nafion<sup>®</sup> solution (Grade: D-520, Alfa Aesar, USA).

S. No.	Nafion <sup>®</sup> details	Type of components/properties	Value
1	<b>Solution components (wt %)</b>	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	<b>Solution properties</b>	Specific gravity	0.92-0.94
		Available acid capacity (meq/g, H <sup>+</sup> polymer basis)	> 1
		Total acid capacity (meq/g) H <sup>+</sup> polymer basis	1.03-1.12
		Viscosity (cP; at 25 °C and 40 per second shear rate)	10-40

**Table 3.3** Properties of PTFE dispersion (Sigma Aldrich, USA).

S. No.	Properties	Value
1	Concentration	60 wt % dispersion in H <sub>2</sub> O
2	Particle size	0.05-0.5 μm
3	pH	10
4	Viscosity	~ 20 cP (lit)
5	Transition temperature	T <sub>m</sub> 337 °C (ASTM D 1475)
6	Density	1.5 g/ml at 25 °C

Polyvinyl alcohol (PVA,  $M_{wt}$  of 89,000–98,000, >99 % hydrolyzed) was procured from Loba Chemie, India for alkaline membrane preparation. The detailed properties of PVA are given in Table (3.4). Glutaraldehyde (Merck, India) was used as a crosslinker. The atmospheric oxygen (air) and pure oxygen were used as cathode oxidant. The typical properties of methanol and ethanol are given in Table (3.5). All the experiments were performed using laboratory prepared distilled water.

**Table 3.4** Properties of polyvinyl alcohol (Loba chemie, India).

S. No.	Properties	Value
1	Chemical formula	$(C_2H_4O)_n$
2	Melting point	200 °C
3	Decomposition temperature	228 °C
4	Density	1.269 g/cm <sup>3</sup>
5	Average molecular weight	89,000 – 98,000 g/mol

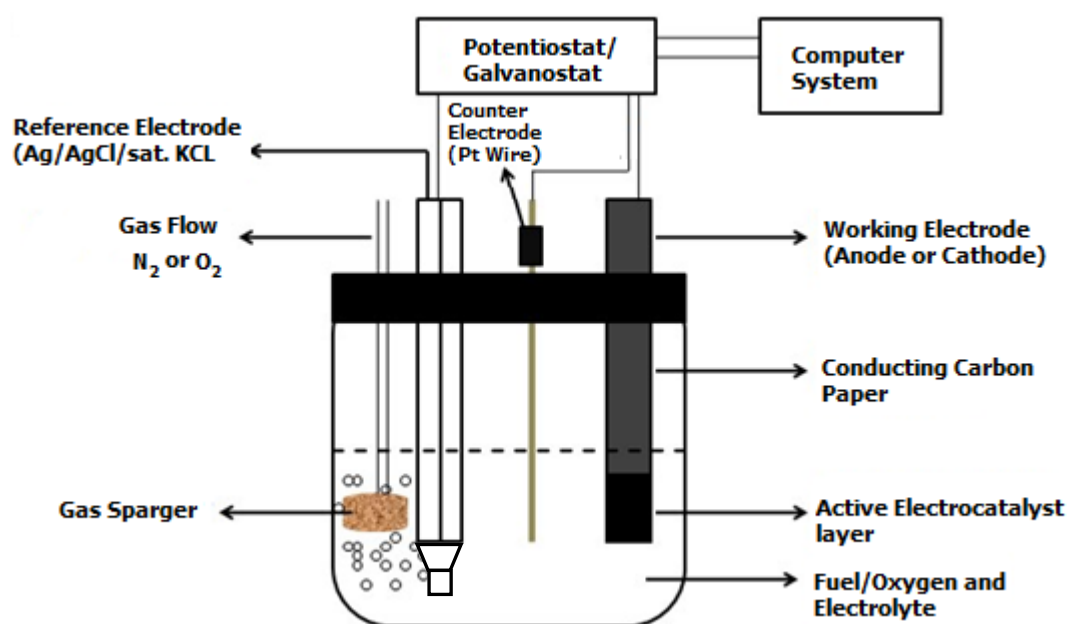
**Table 3.5** Typical properties of the fuels at 1.01 bar and 298 K.

Fuel	Molecular formula	Molecular weight	Energy density (kWh/kg)	Enthalpy of combustion ( $\Delta H$ ) (kJ/mole)	Gibbs free energy of formation ( $\Delta G$ ) (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

## 3.2 Experimental setup

### 3.2.1 Half cell studies

The electrochemical characterizations of prepared anode and cathode were accomplished using a Potentiostat-Galvanostat (PGSTAT 204, Autolab, Netherlands). The half cell analyses of the electrodes were performed in a three-electrode cell assembly to obtain cyclic voltammograms (Fig 3.1). The working electrode was prepared from a long strip of carbon paper whose tip was coated with electrocatalyst ink. The rest of the strip was connected to the outside circuit. The anode was immersed in the fuel and electrolyte (KOH) solution saturated with nitrogen gas which was supplied from the cylinder and purged through the solution using silicon tubing. Nitrogen gas was used to maintain an inert atmosphere in the solution. Similarly, cathode was immersed in oxygen saturated KOH solution to study cathode reduction.



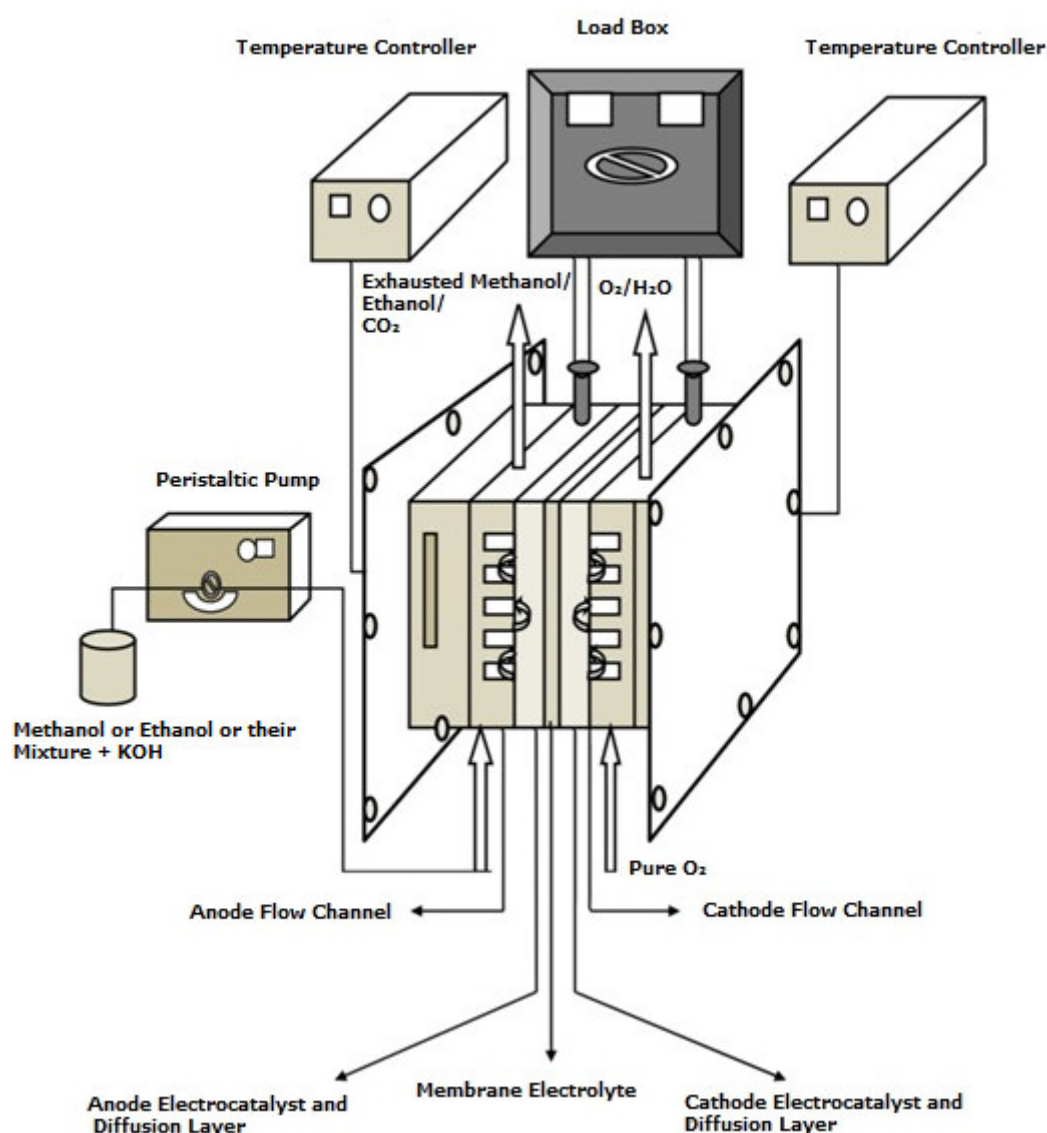
**Figure 3.1** Schematic of cyclic voltammetry setup for single electrode studies.

The potentiostat is an electronic instrument consists of three electrodes e.g., the prepared anode as the working electrode, reference electrode used was Ag/AgCl in saturated KCl and the counter electrode was in the form of long platinum wire (Fig 3.1). The terminals

of the electrodes were connected to a Potentiostat-Galvanostat (PGSTAT) for cyclic voltammetry. The PGSTAT was connected to a computer which recorded all current voltage data and NOVA software was used to generate the voltammograms (Pramanik and Basu 2011).

### 3.2.2 Direct alcohol fuel cell (DAFC)

The performance of the synthesized PVA based alkaline membrane was evaluated using methanol, ethanol and their mixture in a single fuel cell setup (Fig 3.2).



**Figure 3.2** Schematic of direct alcohol fuel cell setup.

Two current collectors with serpentine flow-field were made of graphite (1 mm wide and 1 mm deep) which were fixed outside the membrane electrode assembly (MEA) at both electrodes. Two electric heaters were placed in between current collector and end plates for heating purpose. The end plates were tightened using bolts at uniform torque. The methanol or ethanol or their mixture mixed with KOH solution was fed into the anode using peristaltic pump (Electrolab, India) and humidified oxygen /air was fed to the cathode side. The multimeters (Sanwa, Japan) were connected to the anode and cathode terminals to generate voltage – current (V-I) data for different operating conditions of the fuel cell. The photograph of the experimental setup is shown in Appendix-A (page no.195).

### **3.3 Method**

#### **3.3.1 Preparation of alkaline membrane**

Membranes were prepared from 5 wt % of PVA water solution by three different methods (i) physical crosslinking (ii) chemical crosslinking and (iii) without crosslinking. The membrane by physical crosslinked were obtained after dissolving the solid PVA granules in distilled water at a temperature of 80 °C using a magnetic stirrer to make a 5 wt % of PVA solution. Air bubbles were removed by vacuum. Viscous and bubble free clear PVA solution was gently transferred into the petri plates. The physical crosslinked membranes were obtained by treating the PVA solution loaded petri plates by freeze –thaw method (Zugic et al., 2013 and Gupta and Pramanik 2018). In freeze thaw method, the plates were subjected to 10 cycles of freezing at -8 °C for 18 h and thawing at room temperature for 6 h. The plates were then kept in a vacuum oven at a temperature of 50 °C for 24 h to form a thin film of PVA membrane.

The chemical crosslinked membranes were obtained by directly treating the PVA solution loaded petri plates into a vacuum oven at a temperature of 50 °C for 24 h. Thin films of PVA were carefully peeled off from the petri plates keeping it immersed in distilled water. The PVA membranes were crosslinked with glutaraldehyde (GA) as a crosslinking agent under heterogeneous condition (Yang et al., 2012 and Gupta and Pramanik 2019b). For chemical crosslinking, the membranes were treated in a solution of glutaraldehyde of various concentrations 1 wt %, 2 wt %, 2.5 wt % and 3 wt % containing acetone and hydrochloric acid as a catalyst in the ratio of 1:2:0.01 for 1 h. All crosslinked membranes were subsequently washed repeatedly in distilled water to remove excess chemicals if any.

In another attempt, PVA based membrane was synthesized without any crosslinking. As discussed above, granules of PVA was dissolved in distilled water to make 5 wt % of PVA solution and then the solution was poured in a petri plate. The petri plates were placed in a vacuum oven at a temperature of 50 °C for 24 h. The final form of PVA membrane is known as pristine membrane. The thickness of all the three types of PVA membrane was  $180 \pm 10 \mu\text{m}$ . The synthesized PVA membranes via physical crosslinked, chemical crosslinked and without crosslinked methods were further treated with KOH solution of different concentrations to impregnate KOH within the membrane matrix. The synthesized PVA membrane samples of area larger than MEA ( $6.25 \text{ cm}^2$ ) were immersed in 0 M KOH/water and KOH of various molar solutions at a temperature of 30 °C for 24 h. The KOH doped pristine and crosslinked PVA membranes were further characterized which are discussed in the section 3.3.3, Membrane characterization (page no. 60).



### 3.3.2 Preparation of electrodes and membrane electrode assembly (MEA)

The electrodes i.e., anode and cathode should be properly manufactured to achieve maximum cell performance in terms of power density. The electrodes for direct alcohol fuel cell (DAFC) should be porous in nature to ensure liquid fuel methanol or ethanol or their mixture and oxidant oxygen diffusion through gas diffusion layer (GDL) to the anode and cathode active zones, respectively. The anode was fabricated using Pt–Ru/C (30 % : 15 % by wt) electrocatalyst. The electrocatalyst ink/slurry was prepared by mixing suitable amount of electrocatalyst along with acetylene black carbon, isopropyl alcohol, Nafion<sup>®</sup> ionomer and PTFE dispersion for 15 minutes in an ultrasonic water bath. PTFE, along with pores at the anode provides a flow network which allows easy escape of the reaction products from the anode. Further, the presence of PTFE in the anode decreases the crossover of methanol or ethanol or their mixture from anode to cathode side, which resulting in higher cell performance. The inks were then loaded onto carbon paper/gas diffusion layer of area about 6.25 cm<sup>2</sup> using paintbrush technique. The electrocatalyst painted carbon paper/gas diffusion layer was further dried in a vacuum oven for 1 h at a temperature of 80 °C followed by sintering for 3 h at a temperature of 280 °C to get the final form of anode.

The cathode was fabricated using Pt/C<sub>HSA</sub> (40 % by wt.) electrocatalyst. The electrocatalyst ink/slurry was prepared by mixing suitable amount of cathode electrocatalysts along with acetylene black carbon, isopropyl alcohol, Nafion<sup>®</sup> ionomer and PTFE dispersion for 15 minutes in an ultrasonic water bath. The electrocatalyst ink was painted on GDL and dried similar way as that of anode. The dried cathode was sintered at 280 °C for 3 h to obtain the final form of the cathode.

The membrane electrode assembly (MEA) was prepared keeping the KOH-doped PVA membrane in between sintered anode and cathode followed by hot pressing at a pressure

of 10 kg/cm<sup>2</sup> for 10 min at a temperature of 30 °C. The active area of the developed MEA was 6.25 cm<sup>2</sup>.

### 3.3.3 Membrane characterization

The laboratory synthesized pristine, physical and chemical crosslinked PVA membranes were further optimized with reference to KOH uptake, water uptake and ionic conductivity. The each set of experiments for KOH uptake, water uptake and ionic conductivity were performed three times to check repeatability and reproducibility and the average values of three measurements along with standard deviation are shown in the results. The crosslinked and pristine PVA membranes were also studied for their surface morphology, crystal structure, functional group and mechanical property mainly tensile strength.

#### 3.3.3.1 KOH/Water uptake

The fresh membrane samples were dried overnight at a temperature of 80 °C and pressure of 1 atm. The dry weight ( $W_o$ ) of the membrane samples were measured before doping in KOH solution. After that, the samples were immersed in KOH solution of various concentrations for 24 h. Then, the membranes were gently wiped with tissue paper and weighted ( $W_d$ ). The membranes were then dried overnight at 80 °C and again weighted ( $W_{dd}$ ). Water uptake ( $W_U$ ) and KOH uptake ( $Q_U$ ) of the membranes were calculated as follows:

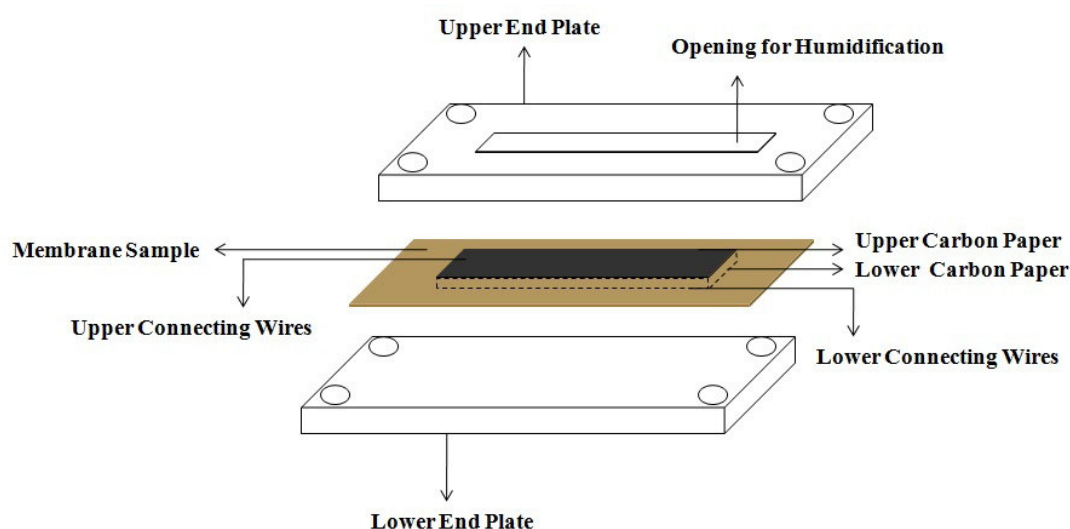
$$W_U = \frac{w_d - w_{dd}}{w_o} \times 100 \quad (3.1)$$

$$Q_U = \frac{w_{dd} - w_o}{w_o} \times 100 \quad (3.2)$$

where  $W_d$ ,  $W_{dd}$  and  $W_0$  are weight of the doped (water + KOH), dried doped (KOH), and dry membranes (water and KOH free), respectively.

### 3.3.3.2 Ionic conductivity measurement

The ionic conductivity of the synthesized membrane was measured by electrochemical impedance spectroscopy (EIS) technique in a PGSTAT 204 (Autolab, Netherland). Prior to measurements, the membrane samples were equilibrated in various molar KOH solutions for 24 h. The membrane sample of area  $5 \text{ cm}^2$  was fitted between two carbon electrodes, to make a two probe, through- plane system, each of surface area  $1 \text{ cm}^2$  as shown in Fig (3.3).



**Figure 3.3** Two probe through plane setup for measuring membrane conductivity.

The AC frequency range was maintained from 100 kHz to 0.1 Hz with amplitude of 10 mV. The ionic conductivity of membrane (S/cm) was calculated using Equation (3.3).

Where  $l$  is the membrane thickness (cm),  $R$  is the membrane resistance ( $\Omega$ ) and  $A$  is the contact area of the carbon electrodes ( $\text{cm}^2$ ).

$$\sigma = \frac{l}{RXA} \quad (3.3)$$

### 3.3.3.3 High resolution scanning electron microscopy (HR-SEM)

The surface and cross-sectional morphologies of the synthesized PVA membranes were visually investigated with a HR-SEM (Nova Nano SEM 450, 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 image is formed on the screen based on the number of electrons (Zhou et al., 2006). The membrane samples were coated with conducting layer prior to the HR-SEM analysis. The membrane samples for imaging were carefully attached on the given circular sample holder. The sample holder was placed in the scanning electron microscope chamber and images were taken at fixed magnification of 500 nm for consistency.

### 3.3.3.4 Fourier transform infrared spectroscopy (FTIR)

The fourier transform infrared spectroscopy (FTIR) was used to characterize the specific chemical groups in the synthesized PVA membrane. FTIR spectroscopy is a non destructive technique for characterization of materials based on the fact that molecules absorb specific frequencies according to their structures. The frequency of bond or groups that vibrate matches with that of absorbed frequency (Singh et al., 2011). FTIR spectra were acquired in the range of the wave number from 4000 to 550  $\text{cm}^{-1}$  using Nicolet iS5 FTIR spectrophotometer (Thermo Scientific, USA). The resolution was kept at 4  $\text{cm}^{-1}$ .

### 3.3.3.5 X-ray diffraction (XRD)

The X-ray diffraction (XRD) is a powerful technique to study the crystal structure of materials. A XRD system consists of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector (Sharma et al., 2012). In the X-ray diffractometer, X-ray beam of a single wavelength is used for analysis of the materials. The incident angle of the X-ray beam is continuously varied and a spectrum of diffraction intensity versus the angle between incident and diffraction beam is recorded (Leng 2009). The crystal structures of the PVA membranes were examined using a RIGAKU (Germany) bench top X-ray diffractometer (XRD) for  $2\theta$  angles between  $10^\circ$  and  $80^\circ$ . The scan rate was fixed at  $5^\circ/\text{min}$ .

### 3.3.3.6 Mechanical properties

The most commonly analyzed mechanical properties for the membrane are Young's modulus, tensile strength, and elongation-at-break (Callister 2007). The above mentioned properties are obtained from evaluating the stress-strain curve. The membrane samples are pulled at a known rate until the sample breaks and the corresponding resistance force is measured. In the present study, the mechanical properties were measured with an INSTRON model 3369 testing instrument (USA) at a temperature of  $30^\circ\text{C}$ . The pristine and crosslinked PVA membrane samples were cut into rectangular shapes of length 4 cm and width 1 cm and were pulled at a crosshead speed of 5 mm/min to measure the tensile strength of the synthesized KOH doped PVA membrane.

### 3.3.4 Scanning electron microscope (SEM) of electrodes

The operating principle of SEM is similar to HR-SEM as discussed in the section 3.3.3.3 (Page no. 62). The major difference between SEM and HR-SEM is based on the type of

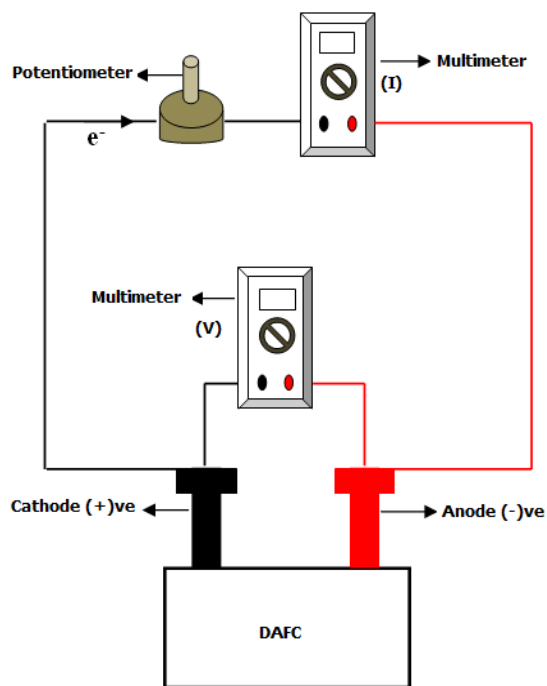
electron emission gun used. The SEM uses thermionic electron emission gun while HR-SEM uses field emission based electron emission gun (Zhou et al., 2006). The sintered anode (Pt-Ru/C) and cathode (Pt/C) of various loading and blank gas diffusion layer (GDL) were visually observed using (SEM) (EVO 18 SEM from Carl Zeiss, Germany) to investigate the surface morphology of the electrodes with reference to electrocatalyst distribution at the electrocatalyst layer.

### 3.3.5 Half cell study

The prepared anode and cathode were tested for their electrochemical activity towards electrooxidation of alcohol fuels and oxygen reduction reaction using cyclic voltammetry (CV) experiments in a three electrode cell assembly. The anode (Pt-Ru/C) was tested for electrooxidation of methanol or ethanol or in some cases their mixture in alkaline medium containing KOH as the alkaline electrolyte. The solution mixture was purged with nitrogen gas for 30 minutes to remove dissolved oxygen gas prior to electrooxidation study. The oxygen reduction reaction was studied using cathode (Pt/C<sub>HSA</sub>) in nitrogen saturated or oxygen saturated KOH solution. The half cell experiments were conducted to study the effect of different parameters such as scan rate, electrocatalyst loading, fuel concentration and electrolyte concentration for the electrooxidation of methanol and ethanol and their mixture. It should be noted that the mixture of methanol and ethanol mixed with fixed KOH concentration were studied only for various molar ratios of methanol to ethanol in the mixture using optimum loading of anode (Pt-Ru/C) electrocatalyst and scan rate of 100 mV/s. In the CV experiments, applied voltage range for anode study was in the range of - 0.8 V to 1 V and -1 V to 1 V for cathode.

### 3.3.6 Single cell study

The polarization and power density data were generated using single direct alcohol fuel cell experiments. The single cell tests were also carried out repeatedly three times. In case of single cell study the time taken to record the data is less under steady state condition. It means the cell reaches steady state in short duration. Therefore, practically no variation is observed when repeating the test. The constructed fuel cell with different types of PVA based alkaline membranes were tested at different cell conditions. The different concentration of methanol or ethanol or in some cases their mixture of various proportions mixed with electrolyte KOH were fed to the anode at a flow rate of 2 ml/min using a peristaltic pump (Electrolab, India). As mentioned above, the mixture of methanol and ethanol mixed with fixed KOH electrolyte were studied only for various molar ratios of methanol to ethanol in the mixture at a temperature of 30 °C and optimum loading of anode (Pt-Ru/C) and cathode (Pt/C<sub>HSA</sub>) for both types of PVA based alkaline membranes. The concentration of KOH was also varied from 0.5 M to 8 M in the same range of CV experiments. The humidified oxygen (80 % relative humidity) was used as an oxidant and passed to the cathode side at a flow rate of 100 ml/min. The DAFC was activated by passing a solution of methanol or ethanol or their mixture mixed with KOH of certain concentration for 1 h to ensure that the anode electrocatalyst layer is completely surrounded by fuel and electrolyte molecules. The steady-state voltage and corresponding current data at different load were measured using the electrical circuit as mentioned in Fig (3.4) to get the polarization and power density curves.



**Figure 3.4** Electrical circuit diagram for recording current-voltage data.

### 3.3.7 Stability test of DAFC

The stability tests of DAFC were conducted for both physical and chemical crosslinked PVA membranes. The time period for evaluation was 15 h at a constant load at a temperature of 30 °C using optimum parameters. The operating cell potential (OCP) was recorded at an interval of 1 h.