CHAPTER 3

EXPERIMENTAL

The materials used for the synthesis of membrane electrolyte, preparation of electrocatalyst and fabrication of direct sodium borohydride fuel cell are discussed in **section 3.1 Materials**. The methods of synthesis of membrane electrolyte, preparation of electrocatalyst slurry for membrane electrode assembly, various characterization methods of membrane electrolyte and electrode, half-cell study and single cell study are discussed in **section 3.2 Methods**.

3.1 Materials

The polyvinyl alcohol (PVA) was used as basic membrane material procured from Molychem, India. The $NaBH_4$ powder was used as anode fuel purchased from SDFCL, Fine Chem Limited, India. The oxidant oxygen was procured from Sigma Gas, India. The sodium hypochlorite (Thermo Fischer Scientific, India) was also used as an oxidant in some experiments. The NaOH (Thermo Fischer Scientific, India) was used as an alkaline medium for the fuel as a supporting electrolyte and doping it in the synthesized membrane to make the membrane electrolyte alkaline for OH^- ion conducting. The solvent isopropyl alcohol was procured from Thermo Fischer Scientific, India. The HCl (35%) used in the preparation of the TEOS mixture was obtained from Merc Life Science Pvt Ltd, India. Tetraethyl orthosilicate (TEOS) was purchased from Sigma-Aldrich, St. Louis, MO, USA. The PTFE treated carbon paper (TGP-H-60) or gas diffusion layer (GDL) and Nafion® (D-520, 5 wt. %) dispersion was obtained from Alfa Aesar, USA. The Polytetrafluoroethylene (PTFE) dispersion (60 wt. %) was obtained from Sigma Aldrich, Germany. The platinum electrocatalyst i.e., Pt (40 wt. %)/High surface area carbon black (C_{HSA}), was purchased from Alfa Aesar, USA.

Table 3.1 Properties of Polyvinyl alcohol (Molychem, India).

Sr. No.	**Properties**	**Value**
1	Molecular weight	approx 125000
2	Degree of hydrolysis	85-89
3	pH of 4 % aq. Solution	5.0 – 8.0
4	Viscosity (4 % aq. soln. at 20°C)	35 – 50 Cs
5	Loss on drying at 110°C	5 %
6	Water insoluble substance	0.1%

Table 3.2 Properties of the TEOS (Sigma-Aldrich, St. Louis, MO, USA).

Sr. No.	**Properties**	**Value**
1	Physical state	Liquid
2	Molecular weight (g/mol)	208.33
3	Density (at 20 ºC) (g/cm^3)	0.933
4	Initial Boiling Point (ºC)	168
5	Viscosity (at 20 ºC) (mPa)	0.6
6	Flash Point (ºC)	45

Table 3.3 Properties of the $NaBH_4$ fuel (SDFCL, Fine Chem Limited, India).

Sr. No.	**Properties**	**Value**
1	Molecular weight (g/mol)	37.83
2	Melting range (°C)	36-37
3	Boiling Range (°C)	500
4	Specific Gravity (water =1)	1.07
5	pH (1% solution)	> 7

3.2 Methods

3.2.1 Synthesis of the NaOH doped pristine PVA-TEOS membrane electrolyte

At first, dry PVA granules were dissolved in water at a temperature of 80 °C to obtain an aqueous 5 wt. % PVA solution and continued stirring for 6 h to get a clear viscous homogeneous solution (Yadav and Pramanik 2023). The silica doped PVA-TEOS membrane composite was prepared by the sol-gel method after getting the PVA viscous solution and subsequently adding the TEOS mixture to the PVA solution. The PVA solution was cooled down to room temperature (25 °C) before adding the TEOS mixture to the PVA solution. It should be noted that the TEOS was added to the polymer by weight of 5 %. A mixture of TEOS was prepared by combining H_2O, HCl, and TEOS in the molar ratio of 4:0.1:1 and then continously stirred for 2 h at ambient temperature for 2 h (Yadav and Pramanik 2023, Kim et al. 2004). The PVA and TEOS mixture was then stirred for 12 h at room temperature to get the homogeneous mixture. The resulting PVA-TEOS homogeneous mixture was poured into a petri dish and allowed to evaporate all solvent at ambient temperature (25 °C) to gets the solid film of PVA-TEOS matrix. The solid membrane was peeled off from the petri dish very carefully. A clear and homogeneous membrane was obtained at the end of the casting (**Figure 3.1**). **Figure 3.1**a shows the photograph of pristine PVA membrane. Whereas, PVA-TEOS composite membrane is shoen in the **Figure 3.1**b.

The resulting membrane was then doped with NaOH solution of varying concentrations ranging from 0 M (pure water) to 7 M to obtain alkaline solid pristine PVA-TEOS composite membrane electrolytes for DSBFC applications. The NaOH doped pristine PVA-TEOS was designated as PVA-TEOS-(0M), PVA-TEOS-(2M), PVA-TEOS-(3M), PVA-TEOS-(4M), PVA-TEOS-(5M), PVA-TEOS-(6M), PVA-TEOS-(7M) for doping with 0 M, 2 M, 3 M, 4 M, 5 M, 6 M, and 7 M NaOH solutions, respectively. The synthesized membranes were further characterized and then tested in a fuel cell for its performance evaluation.

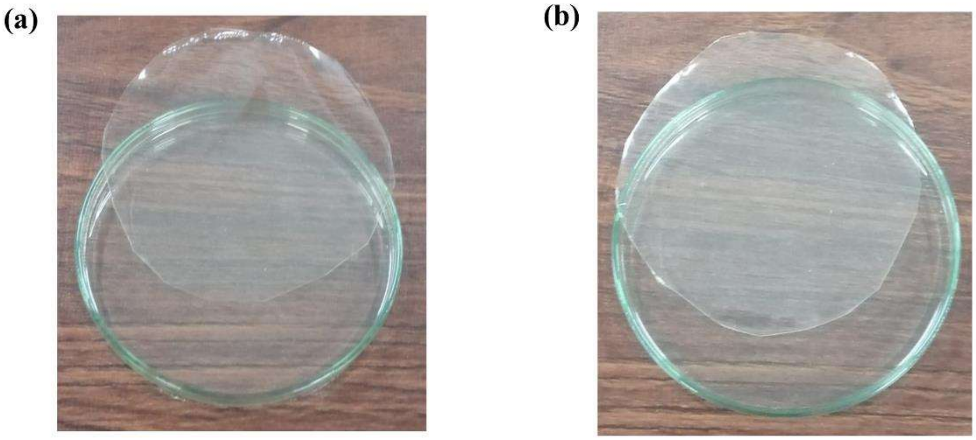


Figure 3.1 Photograph of lab synthesized membrane (a) pristine PVA (b) PVA-TEOS.

3.2.2 Synthesis of the NaOH doped physically crosslinked PVA-TEOS membrane electrolyte

The PVA granules were dissolved and the PVA-TEOS mixture was prepared as described in the previous **section 3.2.1**. The PVA-TEOS solution was poured into petri dish and the physical crosslinking of the PVA-TEOS solution was done by standard freezing-thawing process keeping the solution at -15 °C for 18 h (freezing process) in a perti dish and then keeping it at 30 °C for another 6 h (thawing process) (Gupta and Pramanik 2018, Yadav and Pramanik 2024a). The freeze-thaw cycle was repeated as per the required pre-determined number of cycles to obtain the PVA-TEOS (PT) membrane at the optimized number of freeze-thaw cycles. The physically crosslinked PVA-TEOS (PT) membranes were designated as PT-0Cy, PT-3Cy, PT-5Cy, PT-7Cy and PT-9Cy for pristine membrane (0 cycle), 3, 5, 7 and 9 freeze-thaw cycles, respectively. The membrane was then dried at temperature of 50 °C for 12 h and peeled off from the petri dish. The PVA-TEOS/PT membranes were doped with various concentrations of NaOH to obtain an alkaline membrane electrolyte of varying conductivity. The pristine PVA-TEOS and physically crosslinked PVA-TEOS were designated as PT-0Cy-(X), PT-3Cy-(X), PT-5Cy-(X), PT-7Cy-(X) and PT-9Cy-(X) after doping with various concentration of NaOH (where X denoted as 0 M, 3 M, 4 M, 5 M, 6 M, 7 M and 8 M). It should be noted that TEOS loading in the PVA solution was also varied from 5 wt. % to 15 wt. %. Accordingly, the membranes were further designated like $PT_{Wwt.\%}$-nCy-(X), (Where '$W_{wt\%}$' is weight percentage of TEOS in PVA, 'n' is number of the freeze-thaw cycle, varies from 0 (pristine) to 9 and 'X' is the doping concentration of NaOH).

3.2.3 Characterization of membrane electrolyte

3.2.3.1 Water uptake, NaOH uptake, swelling ratio

To determine the water uptake and NaOH uptake, the fresh membrane was dried at temperature of 80 °C for 12 h. The dried weight membrane was designated as W_o and it was further doped with various concentrations of NaOH for 24 h. The membrane was wiped out gently with tissue paper to remove excess surface water and NaOH from the membrane surface. The NaOH doped membrane was weighted and designated as W_d. The NaOH doped membranes were then weighed again after drying at 80 °C for 12 h and designated as W_{dd}. The method of determination of water uptake (W_u) and NaOH uptake (N_u) were taken from the literature (Yadav and Pramanik 2023, Gupta and Pramanik 2019a) and given by the following equations (Equation 3.1 and Equation 3.2):

$$W_u = (W_d - W_{dd}) \times \frac{100}{W_o} \tag{3.1}$$

$$N_u = (W_{dd} - W_o) \times \frac{100}{W_o} \tag{3.2}$$

The weight of the doped membrane (with water + NaOH), dried doped membrane with (NaOH), and dry membrane (without water and NaOH) are denoted by W_d, W_{dd}, and W_o, respectively. The swelling ratio of the synthesized membrane is also an important parameter which is directly affected by the uptake of the membrane. To determine the swelling ratio, the membrane was put into an oven at 80 °C for 12 h ato dry the membrane and then it is equilibrated in distilled water for 24 h at room temperature of 30 °C. The swelling ratio of the membrane is calculated by the following Equation 3.3 (Cali et al. 2020):

$$\text{Swelling ratio}\,(\%) = \frac{(T_{wet} - T_{dry})}{T_{dry}} \times 100 \qquad 3.3$$

T_{wet} and T_{dry} are the wet and dried thickness of the synthesized membrane, respectively.

3.2.3.2 Ion exchange capacity (IEC)

The ion exchange capacity of the membrane sample was determined by dipping the membrane sample in various concentrations of NaOH for 24 h. Then, the membrane sample was washed with distilled water several times to remove excess NaOH from the membrane sample and equilibrated with distilled water. The membrane sample was then dried in an oven for 6 h at a temperature of 40 °C. The membrane was equilibrated for 24 h in 50 ml of 0.01 M HCl aqueous solution, and the ion-exchange capacity was determined from the decrease in acidity, which is calculated by back titration. Back titration involves the neutralization of the solution containing membrane by titration with a 0.01 M NaOH solution using phenolphthalein as an indicator (Gupta and Pramanik 2018, Wang et al. 2020). The area of the membrane sample was 1 cm^2. The following formula was used to determine the ion exchange capacity (Equation 3.4):

$$\mathrm{IEC} = \frac{(V_{HCl} - V_{NaOH})}{M_d} \times C \tag{3.4}$$

Where V_{HCl}, V_{NaOH}, M_d and C are the volume of initially taken HCl (ml), the volume of NaOH consumed in back titration (ml), the mass of the dried membrane (g), and molar concentration of HCl and NaOH (mol/lit), respectively.

3.2.3.3 Ionic conductivity

The ionic conductivity of the synthesized membrane electrolyte was measured by electrochemical impedance spectroscopy (EIS) technique. The electrochemical impedance spectroscopy (EIS) of the membrane electrolyte was performed using a two-probe, through-plane system to measure the ionic conductivity of the synthesized membrane (Yadav and Pramanik 2023, Gupta and Pramanik 2019a). Two pieces of carbon paper, each with a surface area of 1 cm^2 (1 cm × 1 cm), were used to create a sandwiched between two probe system configurations with a membrane electrolyte sample that had a sample size of 6 cm^2 (2 cm × 3 cm) (**Figure 3.2**).

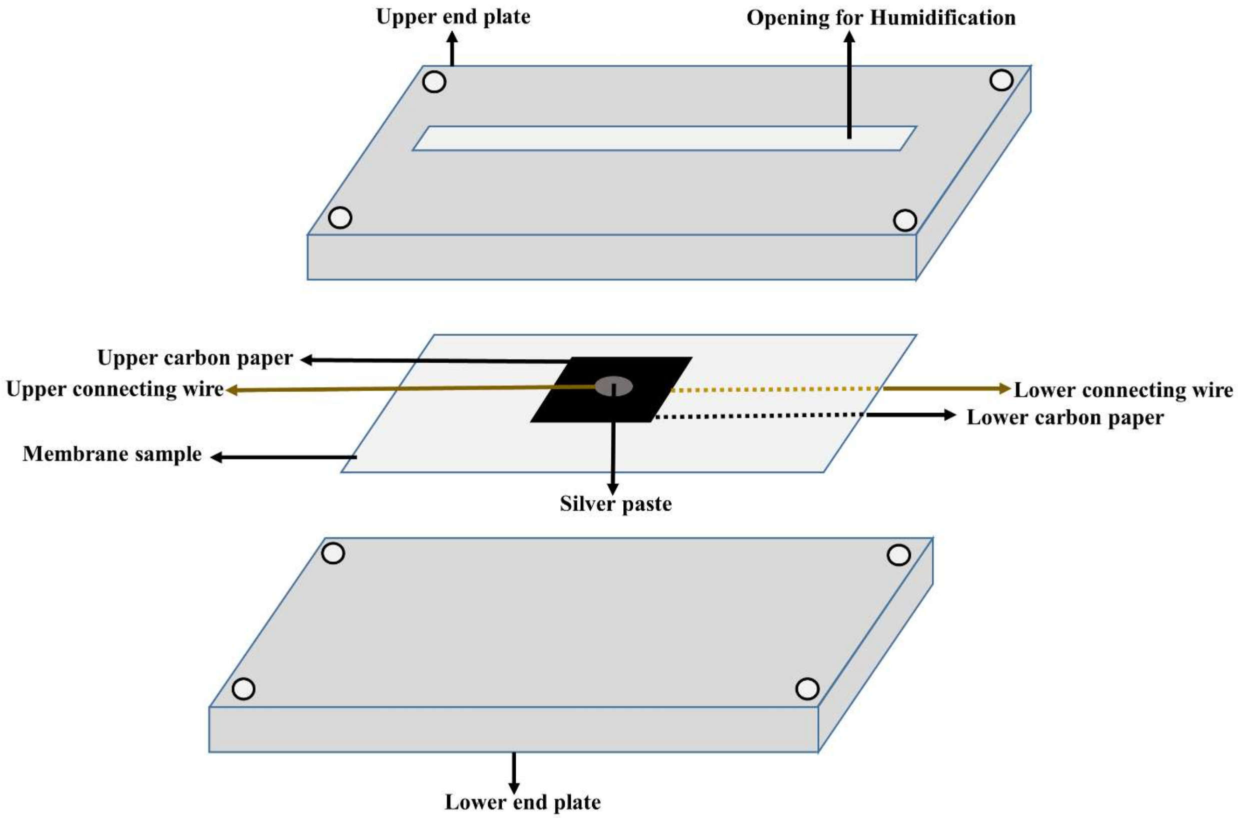


Figure 3.2 Schematic of the two probes through plane setup for the EIS measurement of the membrane electrolyte.

The two-probe setup was attached with an electrochemical analyzer (PGSTAT 204, Autolab Netherland) to study the electrochemical impedance spectroscopy (EIS) of the synthesized membrane electrolyte under the AC frequency ranging from 100 kHz to 0.1 Hz at a voltage amplitude of 100 mV. The ionic conductivity of the membrane electrolyte was calculated using Equation 3.5.

$$\sigma = \frac{l}{R \times A} \tag{3.5}$$

Where l is the thickness of the membrane electrolyte (cm), R is its resistance (Ω) and A is the area between carbon electrodes and membrane (cm^2).

3.2.3.4 X-ray diffraction (XRD) analysis

The crystallinity of the synthesized pristine and physically crosslinked membrane electrolyte was examined by X-ray diffraction (XRD) analysis. The addition of inorganic filler (such as TEOS) and crosslinking results in a change in crysatallinity, which is assessed by the XRD analysis. The equipment used for the XRD analysis was RIGAKU, Japan benchtop X-ray diffractometer. The sample for the XRD analysis was cut into uniform size of 1 cm × 1 cm. The 2θ range of diffraction angles were varied from 20^o to 80^o at a scan rate of 5^o min^{-1} with a 0.02^o angular resolution.

3.2.3.5 Fourier transform infrared spectroscopy (FT-IR) analysis

The distinctive chemical groups in the synthesized pristine PVA, pristine PVA-TEOS and physically crosslinked PVA-TEOS membranes were characterized using FT-IR. The FT-IR spectra of all synthesized membrane electrolytes were obtained using a Nicolet iS5 FT-IR spectrophotometer in the wave number range of 4000 to 500 cm^{-1} (Thermo Scientific, Waltham, MA). The sample for the FT-IR analysis was cut into a uniform size of 1 cm × 1 cm. The various functional groups present in the synthesized membrane viz. -OH, CH, C-O, Si-O-Si, Si-O, and Si-O-C were detected.

3.2.3.6 Scanning electron microscopy (SEM) analysis

The surface morphology of the synthesized membrane was examined by scanning electron microscopy (SEM) analysis. The SEM analysis is an effective method to analyse the membrane surface on a nanometer to micrometer scale. The image is obtained by the interactions between the electron beam and the specimen. The equipment used was Nova Nano SEM 450, FEI Company, USA, which is a field-emission scanning electron microscope (FE-SEM). The surface morphology of the synthesized membrane was investigated by scanning electron microscopy using SEM Quanta 200 F, USA, in some other experiments. The sample size 1 cm × 1 cm was used for each test.

3.2.3.7 Mechanical strength test

The mechanical strength of the synthesized membrane electrolyte mainly tensile strength was measured by ASTM D0882 using UTM AEC1112-ACD, Asian Engineers Company, India. The thickness of the synthesized membrane was measured using vernier caliper. The testing speed was 3 mm/min.

3.2.4 Electrode and membrane electrode assembly (MEA) preparation

The Pt (40 wt. %)/C_{HSA} electrocatalyst was used for both the anode and cathode electrode. Both the electrodes were made by painting electrocatalyst slurry on a gas diffusion layer (GDL), i.e., PTFE treated Toray carbon paper (TGP-H-60). The electrocatalyst used was commercial Pt (40 wt. %)/C_{HSA} on both electrodes. The electrocatalyst slurry was prepared by mixing the appropriate quantity of electrocatalyst, PTFE dispersion, Nafion® ionomer, and isopropanol as diluent. This mixture was sonicated for half an hour using an ultrasonic water bath. The painted GDL was put in an oven for 1h at a temperature of 80 ^{o}C to remove excess solvent. Then, the resulting dried anode and cathode electrodes were sintered in a vacuum oven at 280 ^{o}C for 3 h. The sintering was done to obtain an active and porous structure of the electrocatalysts layer. The active area of the electrodes was 6.25 cm^2 (2.5 cm × 2.5 cm) at the anode and cathode. The photograph of prepared electrode for single cell is shown in **Figure 3.3**a. The NaOH doped synthesized membrane electrolyte was placed between the electrodes, namely the anode and cathode and assembled by clamping method to make the membrane electrolyte assembly (MEA) (**Figure 3.3**b). The electrode for half-cell analysis was prepared using a method similar to that of the single cell anode, except for the size of the electrode. The electrocatalyst ink was painted on the tip (0.5 cm × 1 cm) area of a long strip GDL. The painted electrode was dried in an oven for 1 h at the temperature of 80 °C. The dried electrode was sintered similar way as that of single cell electrode whicgh has already been discussed earlier. The photograph of prepared electrode for half-cell is shown in **Figure 3.3**c.

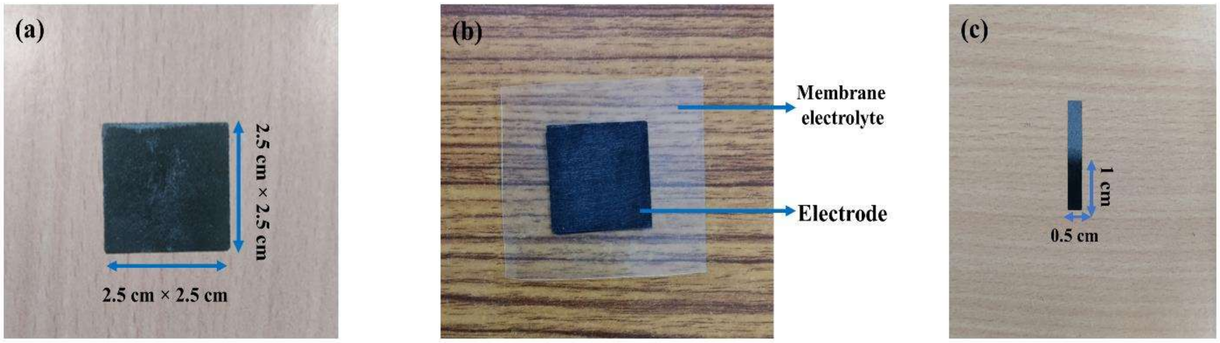


Figure 3.3 Photograph of the prepared (a) electrode for single (b) MEA and (c) electrode for half cell.

3.2.5 Half-cell studies

The single electrode analyses of the individual anode employed in DSBFC experiments were done using cyclic voltammetry (PGSTAT 204, Autolab Netherland). The tip of the fabricated anode electrode was dipped in $NaBH_4$ solution mixed with NaOH and the remaining portion was connected to the external circuit of the PGSTAT (Autolab). The loading of the anode electrocatalyst Pt (40 wt. %)/C_{HSA} was 1mg/cm^2. The electrodes used in the half cell analysis were working electrode, counter electrode and reference electrode. There are various types of reference electrode available such as saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the silver/silver chloride electrode (Ag/AgCl) (Rountree etl. 2014). The reference electrode used in the current research work is Ag/AgCl saturated in KCl solution. The upper and lower voltage were varied from -1.0 V to 1.0 V (Pramanik anf Rathoure 2017) and the scan rates were varied in between 10 mV/s to 50 mV/s (Aytac et al. 2011). The PGSTAT was connected to a computer, which collected all current-voltage data and generated the voltammograms using the NOVA 1.10 software (**Figure 3.4**).

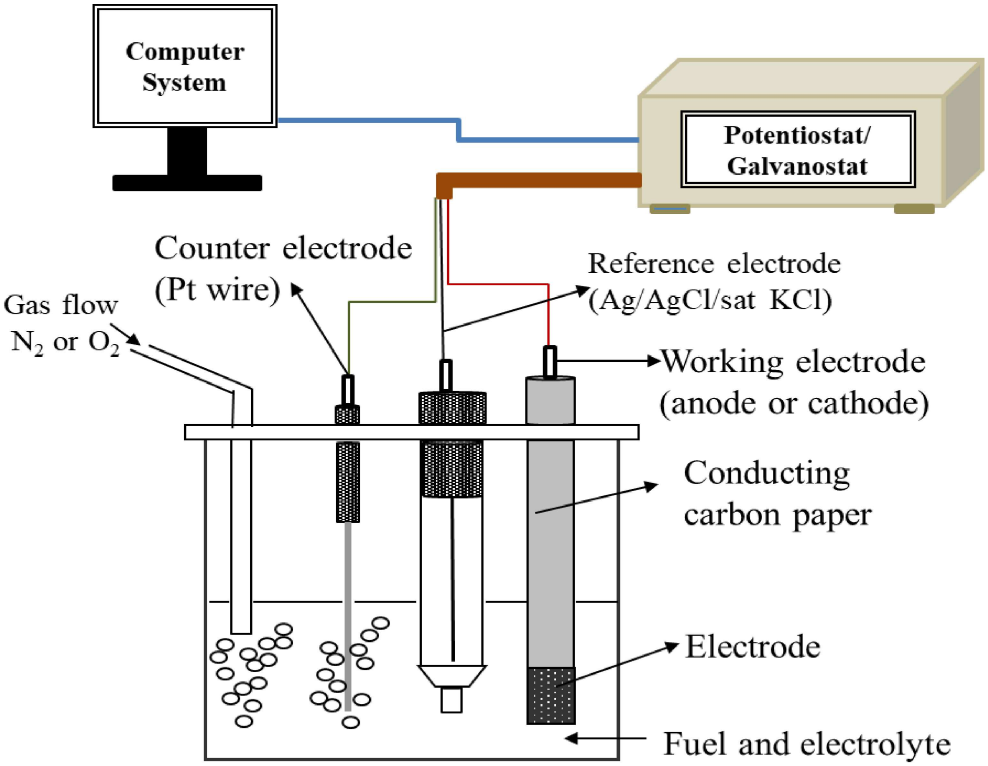


Figure 3.4 Schematic of three electrodes half -cell set-up.

For the cathode study, the electrolyte solution was prepared by dissoving suitable quantity of NaOH in the distilled water and then oxidant oxygen was purged for 20 min to dissolve oxygen in the electrolyte solution. Then the manufacture electrode was immerged in the electrolyte solution for CV studies. Similarly, CV study of cathode electrocatalyst using NaOCl mixed in NaOH solution as oxidant was done.

3.2.6 Single Cell Study

The performance study of the synthesized membrane was conducted using direct sodium borohydride fuel using $NaBH_4$ in NaOH solution as fuel and humidified oxygen as an oxidant. The performance study of sodium hypochlorite (NaOCl) as the oxidant in DSBFC was also studied using the best synthesized membrane.

3.2.6.1 Performance study of the membrane electrolyte in DSBFC using O_2 as oxidant

The single cell test of alkaline direct sodium borohydride fuel cell was performed to study the performance of the synthesized NaOH doped pristine or physically crosslinked PVA-TEOS alkaline membrane. The membrane electrode assembly was made by clamping method, keeping the synthesized PVA-TEOS alkaline membrane in between dry sintered electrodes, i.e., anode and cathode, as per the manufacturing method discussed in **section 3.3.4.** The MEA was clamped between two graphite flow channels/current collectors using four nut bolts at four corners of two end plates located at the extreme outside of the cell assembly.

The two gold plated copper current collectors were placed between the end plates and current collector at the anode and cathode side both. The DC electronic load was connected across these two gold plated copper current collectors to obtain the voltage and current data from the single DSBFC. The schematic of the assembled DSBFC system is shown in **Figure 3.5**a. The alkaline sodium borohydride fuel i.e., $NaBH_4$ mixed in NaOH, was passed to the anode side and pure oxygen was supplied at the cathode side of the DSBFC. The actual photograph of the experimental setup is shown in the **Figure 3.5**b.

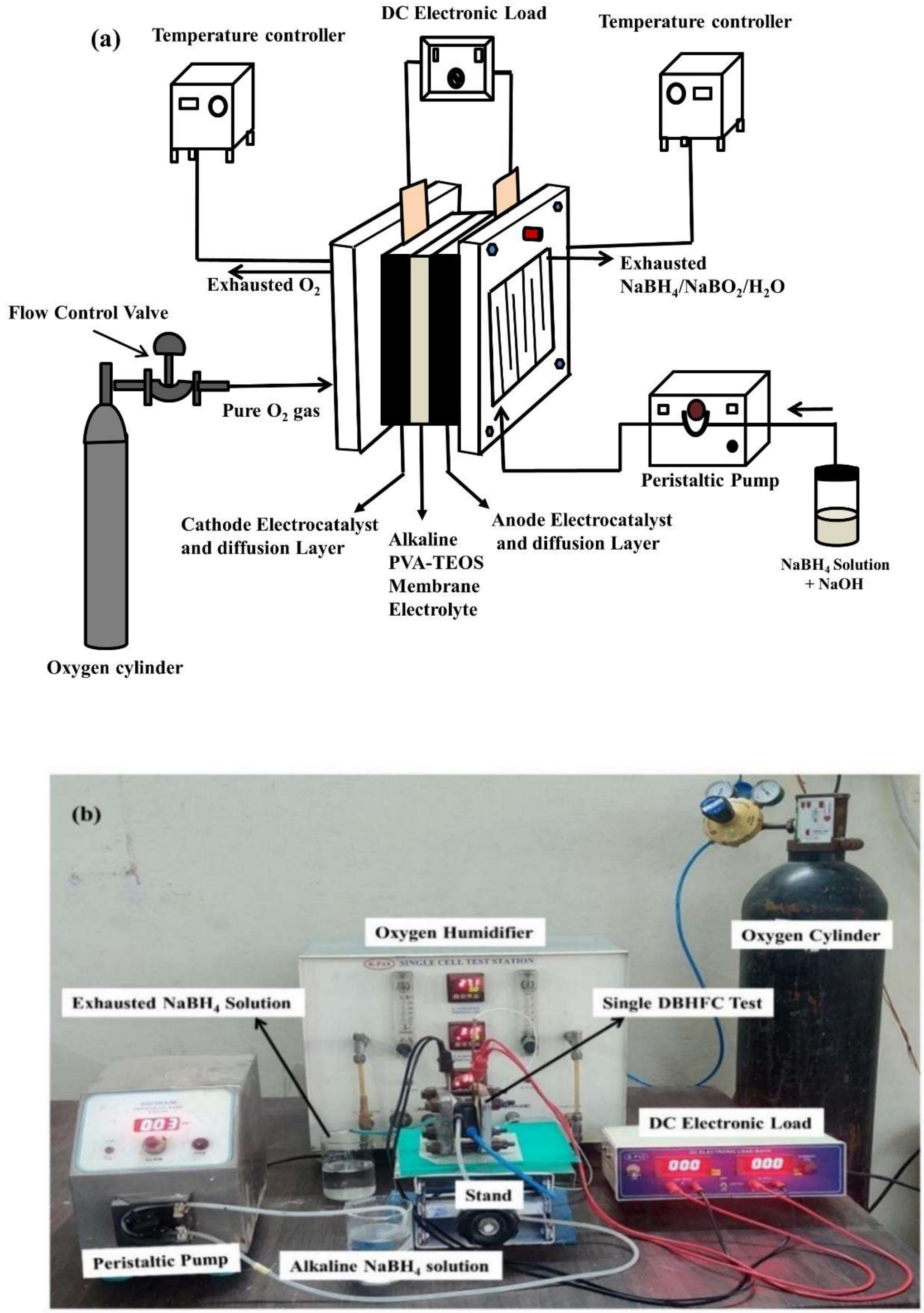
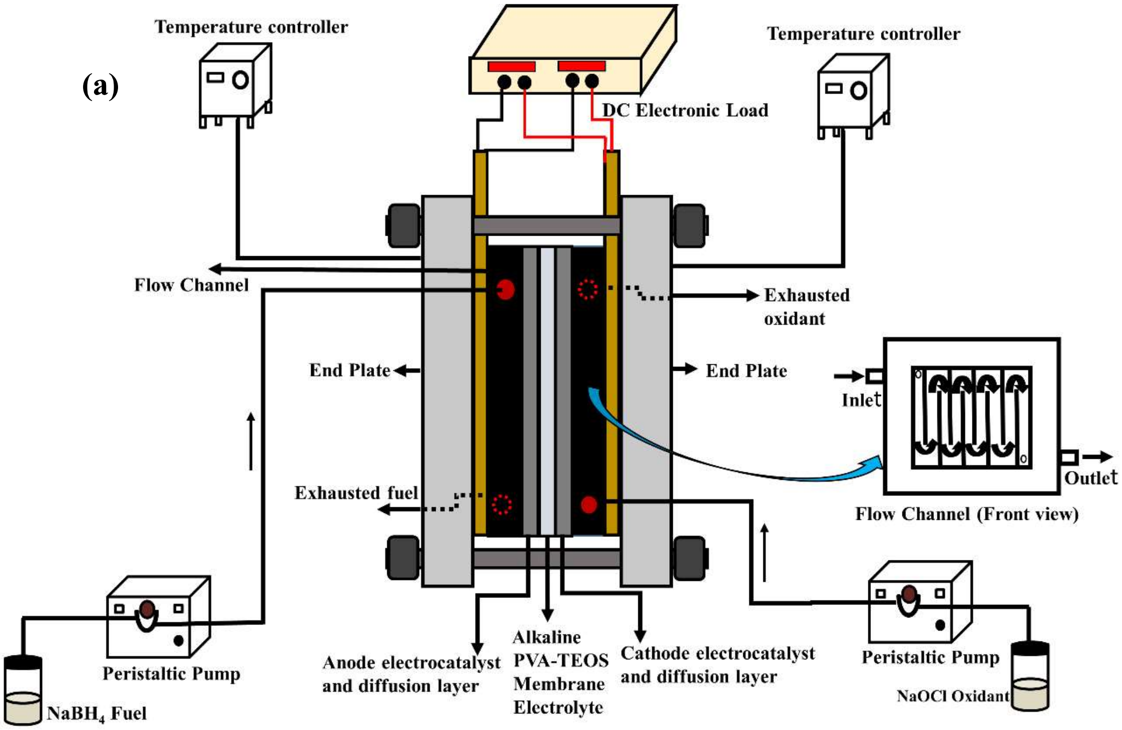


Figure 3.5 (a) Schematic of the single direct sodium borohydride fuel cell (DSBFC) experimental setup (b) the pictorial view of DSBFC experimental setup.

3.2.6.2 Performance study of the membrane electrolyte in DSBFC using NaOCl as oxidant

The single fuel cell test was done in the DSBFC set up to study the effect of NaOCl mixed in NaOH solution as an oxidant using best synthesized membrane electrolyte. **Figure 3.6**a show the two-dimensional schematic of the DSBFC. The assembly of the DSBFC was the same as discussed in the above **section 3.3.6.1**. The fuel $NaBH_4$ mixed in NaOH was passed to the anode side and the oxidant NaOCl mixed in NaOH was passed to the cathode side with the help of a peristaltic pump at the required flow rate (**Figure 3.6**a). The actual photograph of the experimental setup is shown in **Figure 3.6**b.



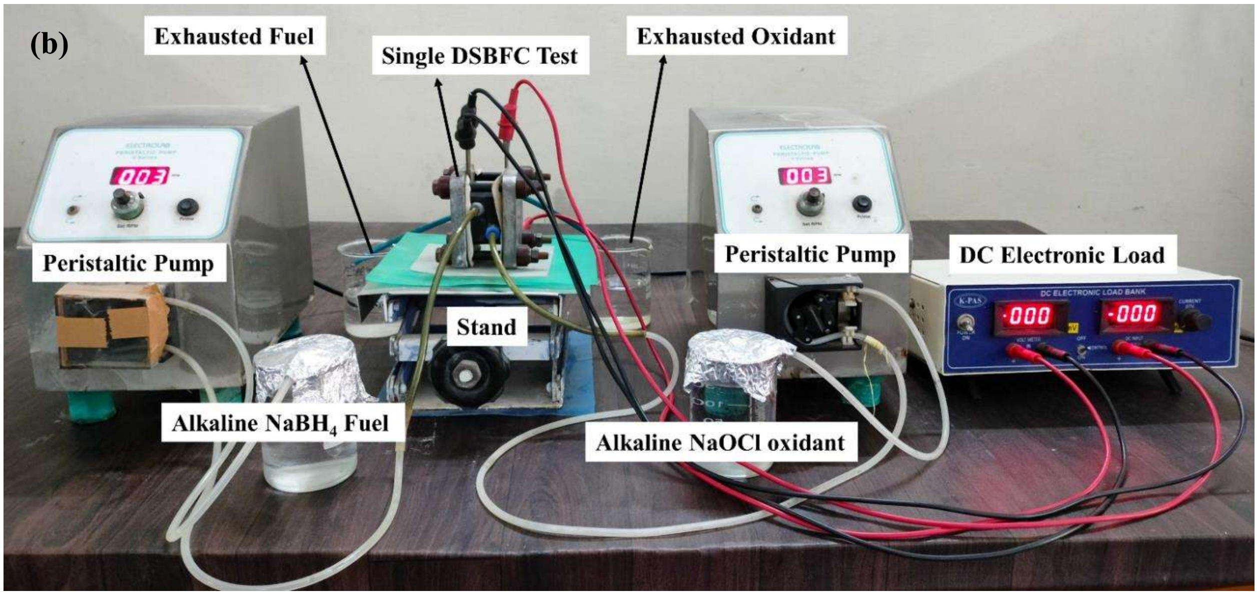


Figure 3.6 (a) Schematic of the single direct sodium borohydride fuel cell (DSBFC) setup (b) the pictorial view of DSBFC experimental setup.