SYNTHESIS AND STUDIES OF NOVEL PROTON EXCHANGE MEMBRANES AND THEIR APPLICATION IN MICROBIAL FUEL CELL

A Major – II Project Report submitted for the partial fulfillment of the award for the degree of

MASTER OF TECHNOLOGY
IN
POLYMER TECHNOLOGY

Submitted by
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DECLARATION

I**,** Brajesh Kumar Tiwari**,** hereby declare that the thesis entitled **"Synthesis and studies of novel proton exchange membranes and their application in Microbial Fuel Cell"** is an authentic record of research work done by me under the supervision of Dr. Richa Srivastava, **Assistant professor,** Delhi Technological University**.** It has not been copied from any source without giving its proper reference, except where due acknowledgement has been made in the text. This work has not been previously submitted for the award of any degree or diploma of this or any other University Institute.

Brajesh Kumar Tiwari
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CERTIFICATE

This is to certify that the project report entitlked **“Synthesis and studies of novel proton exchange membranes and their application in Microbial Fuel Cell”** submitted by Brajesh Kumar Tiwari (Roll No. 2K13/PTE/05) in partial fulfillment for the award of degree of Masters of Technology in Polymer Technology to Delhi Technological University, Delhi – 110042, is the students own work carried out by him under my supervision. The project embodies the original work done by him to the best of our knowledge and has not been submitted to any other degree of this or any other university. The matter embodied in this project report is original and not copied from any source without proper citation.

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ABSTRACT

In present day proton exchange membrane have essential application in electrochemical cells which replace the salt bridge as well as liquid electrolyte by a single polymeric proton exchange membrane. Advantage included as high energy density leak proof high electrical conductivity and thermal stability. PVC is water insoluble polymer and literature survey reveals that its water uptake properties are increased by addition of SiO_2. In the present work, various membranes were prepared by using different concentrations of SiO_2 and their corresponding water uptake was studied. For increasing the conductivity, citric acids (amla juice and lemon juice),and phophotungestic acid (PWA), a heteropolyacid, has been used here. The ion exchange capacity of resulting membranes was carried out by simple titration. Surface morphology was studied by SEM and tensile strength of the prepared samples was calculated. For the fuel cell usage the OCV curve, Polarization curve and the Power density curve was plotted to check the efficiency of the membranes. The power density obtained in case of these membranes showed encouraging results as proton exchange membranes. This work ultimately results into developing membranes using easily available and low cost materials resulting into cost reduction.

CHAPTER 1

INTRODUCTION

A fuel cell is an electrochemical device that converts the chemical energy into electrical energy through redox reactions. The basic components of a typical fuel cell are anode, cathode and an electrolyte (through which protons move between two sides of the fuel cell). A Microbial fuel cell (MFC) is bio-electrochemical type of fuel cell which converts the chemical energy present in organic compounds to electrical energy. Here, the anode reaction is controlled by microorganisms. In MFCs, bacterial energy is directly converted to electricity [1]. It produces a very low power density for industrial applications [2]. These systems are generally considered to be a justifiable new technology [3–4]. These types of cells can be used for bio hydrogen production [5–7] wastewater treatment [8] environmental sensors [9] and bioremediation [10]. The two-chambered configuration can be widely applied for different purposes [11,12] Two-chamber MFCs contain anode and cathode chambers partitioned by a separator [13]. Bacteria in the anode chamber oxidize substrates and transfer electrons to the external circuit through the anode, while protons produced at the anode chamber migrate across the separator to the cathode [14–16]. The separator is one of the most important factors in an MFC, and it has a significant effect on its performance. A proton exchange membrane (PEM) is the most frequently used separator in MFCs due to its moderately high conductivity to cations and low internal resistance compared to other separators [17,18]. Cation exchange membranes (CEMs), also known as PEMs, are one of the most widely used separators and are designed for transferring protons in MFCs [19]. The performance of PEMs is judged according to its ability to transport protons (anode to cathode), and, moreover, they must prevent the transfer of oxygen, substances and minerals from the anode to cathode chambers [15, 20–23]. However, the membrane type (PEM or CEM) has an effect on the MFC performance and has not been studied in depth. Poor proton transferability is one of the most substantial deficiencies in PEMs, which remains significant despite PEMs various positive traits like composition, internal resistance and conductivity. There are some drawbacks which are listed below: (1) PEMs are expensive. The estimated cost of PEMs is reported to be close to 40% of the total cost of a finished MFC [24] (2) Chemical and biological fouling, which results in an increase in internal resistance, will, in turn, result in lower efficiency and performance of MFCs. (3) Higher transfer ratio of cations to protons, which can prevent electrochemical reactions in the cathode, results in lower cathode cell performance. This research reflects a state-of-the-art review on the effect of PEMs in MFC performance observed in certain previous studies with an emphasis on recent advances in PEM designs. The proton exchange membrane fuel cell have advantage over electrochemical cell because its do not emitted polluting gases like CO, SO_2 etc. This is serious drawback for global warming problems which reduces by using proton exchange membrane fuel cell (PEMFC) [25]. It is a low cost and highly efficient device which provides a constant power over long period. Now-a-days, various research groups are focusing on development PEM based fuel cell commercially which will be able to reduce the use of present oil and gas based fuel and decrease the pollution. It's having potential to replace the internal combustion based fuel in vehicles and provide the suitable power for applications. PEM is a solid electrolyte which have H^+, $H3O^+$, $^+NH_4$ as protons carrier there for PEM is an interesting device due to their potential application in ionic devices like fuel cell and electro chromic devices [26-30]. The PEM has properties like high photonic conductivity, low electronic conductivity and high tensile strength, should be non permeable for fuel such as gas or liquids and also having good hydrolytic and oxidative stability. The polymer gel electrolyte is able to conduct electricity in solid as well as aqueous medium. There are various type of work performed on electrolyte that results into six different types of electrolyte viz. **1** conventional dry solid polymer electrolyte**, 2** plasticize solid polymer electrolyte, **3** rubbery electrolyte**, 4** polyelectrolyte**, 5** gel polymer electrolyte and **6** composite polymer electrolyte. Among them, the gel polymers are most widely used because its permeable for H^+ and Li^+ and also having cheap in cost [31-34]. The protons conductivity of PEM can be increased by addition inorganic or organic fillers like carbon nanotube fullerene carbon nanofibre, grapheme have emerged to enhance the mechanical properties as well as proton conductivity of PEM,however addition conductive carbon materials cause the adverse effect with the performance of PEMs [35]. There are two type of ceramic fillers are used in polymer matrix such as active fillers which able to increased the conductivity of PEM membrane example Li_2N, $LiAl_2O_3$, passive filler which do not participate in conductivity, only increased the porosity as well as water up take properties, for example Al_2O_3, SiO_2, MgO. PEM show favorable properties large scale applications example nafion is perfluorinated compounds containing sulphonic acids as functional group is always large scale applications but it's have less applications in small scale applications because due to their high cost and difficulty to prepared in form of micro structure [36-37]. The mechanical properties and conductivity of PEM are can be controlled by designing the porous structure of polymer membrane by using an electrolytic solutions, the conductivity of the porous membrane can be increased by soaking them in to a electrolytic solutions. The porous membranes are able to retained high amounts of electrolytes and provide good mechanical and electrical properties. The performance of electrochemical commercial scale fuel cells are directly depends upon the electrode area. It consists two pieces of electrodes at which oxidation and reduction occurs simultaneously on increasing the electrode area the performance are increases. Due to less pollutant and eco friendly in nature PEM fuel cells are focus on small scale and automotive applications the PEM is type of ionomers which permeable to protons only it is drawback for because it is highly water dependent in nature. The porous structure of protons exchanger consist of millions of capillaries with constant radius which able to transfer itself protons and electrolyte (water) between the electrodes which charge density can be determine by using double layers technique. In the present work we used PVC as polymer for preparation PEM because it is in soluble in water and having ability to formation of thin films which having good mechanical properties [38-40]. Whereas, lemon, amla juice and Phosphotungstic acid are used as for increasing conductivity [41]. One pieces of lemon is able to produce (0.95V) of electricity where as one piece of amla was able to produce (0.90V) of electricity when it is connected by two metals electrode such as copper and zinc, where as conductivity of film are increased in excess amount by addition of Phosphotungstic acid (PWA) [40]. The solvents uptake properties increased by addition of silicates in its with different concentration the water uptake properties are calculated in terms of ion-exchange capacity which basically found in maximum in lower concentration of silicates.The nafion based PEM are applicable up to the temperature 90 °C because at higher temperature it emitted the harmful gases like CO this problem can be minimized by using PBI based PEM its increase the temperature stability up to (120-200 C) and also decrease the emission of CO. The polymer gel electrolyte can be prepared by any of following methods.

Solution cast method: The is the easiest way of preparation for polymer gel electrolyte. In this method, the calculated amounts of polymer and salts are dissolved in polar solvents and the solution is stirred on magnetic stirrer. After complete dissolution, the solution is poured into petri plates. For evaporation of solvents, leave it for few days after which a solid polymer electrolyte is obtained.

Hot press technique It is very fast method as compared to solutions cast method. In this process any external solvents are not used. Hence it is known as dry process. In this process both salts and polymer are taken in powdered form in desired amounts and mixed by using mortars and agate. Mixture is then heated up to the melting points of polymers and a soft lamp is formed which is kept between two cold metals block and pressed for characterization which form a stable polymer electrolyte.

Gelations methods: In this the calculated amounts of salts is added in polar solvent and stirred continuously by magnetic stirrer. After complete dissolution, the polymer are added and stirred again for certain time before pouring them on petri dish and left for some hours for formations of gelation.

The low cost PEM can be prepared by using radiation grafting method by following three steps 1 irradiation to fluoro polymer base films, 2 grafting of styrene from radicals, 3 sulfonated of grafting films. It is found that the polyphosphazene based co polymers have highest proton conductivity which equal to (0.14)S/cm at 80^0C under fully hydrated conditions because its contains pendant alkyl sulphonic acids groups as proton exchange membrane. It is observed that the ion exchange capacity is directly proportional to proton conductivity. The sulphonated aromatics hydrocarbons have IEC 1.9 meq and proton conductivity 0.161 S/cm [42]. While during hydration the IEC increase more than 2meq. The maximum tensile strength and maximum elongation are observed in sulphonated polymer because sulphonic groups have strong ionic interaction hence it's also increase the interaction between molecular chains decrease the movements of chain and enhance the mechanical properties compare to other non sulphonated polymers the maximum tensile strength observed for sulphonated polymers are 1,29 MPa, for sulphonated loaded polymers are 1,65 MPa while in case of silica loaded membrane the tensile strength are lowered [0.73MPa] compare to non silica loaded membrane [0.75MPa] this is because non homogeneous distributions of silica in membrane [43]**.** The ion-exchange capacity and tensile strength of observe som PEM are listed in the table

Phophotungestic acid (PWA) is a inorganic acids which act as strong electrolyte having structural formula $H_3PW_{12}O_{40}nH_2O$. It is observed that the (60% by wt) in aqueous solution behave as good conductor. There for as electrolyte this concentration is most suitable for fuel cell application. Due to this properties PWA is suitable for preparations PEM application for increasing its conductivity [44].

The ion exchange capacity of some known membranes and materials are given below

Table 1: For ion-exchange capacity

S.N.	TYPEOF PEM	DOPANT	I.E. meq/gm
1	Sulphonated aromatic hydrocarbons [42]		1.9
2	Sulphonated aromatic hydrocarbons [42]	During hydrations	2.0
3	PVDF supported silica immobilize [44]	Si-PWA [0.5/1.5]	0.68/0.85
4	PVA composite silica immobilize [40]	Si-PWA	0.90
5	Blend of vinylacetate-acrylicester & styrene-acrylic ester [43]	Sulphonated membrane	0.7

Table2: For tensile strength

S.N.	TYPEOF PEM	DOPANT	TENSILE[MPa]
1	Blend of vinylacetate-acrylicester & styrene-acrylic ester [43]	1sulphonated 2sulphonatedloaded 3 silica imoblize	1(1,29) 2 (1,65) 3 (0.73) /(0.75)
2	PVA composite silica immobilize [40]	Si-PWA	93
3	Blend of vinylacetate-acrylicester & styrene-acrylic ester [43]	Sulphonated membrane	129

4	PVDF supported silica immobilize [44]	Si-PWA[0.5/1.5]	52.6
5		Nafion based	32

Citric fruits like amla or lemons are able to produce electricity itself because its contain strong electrolyt. Amla contain ascorbic acid and lemon contain citric (2-hydroxy,propane-1,2,3-tri carboxyacides) Fig 1

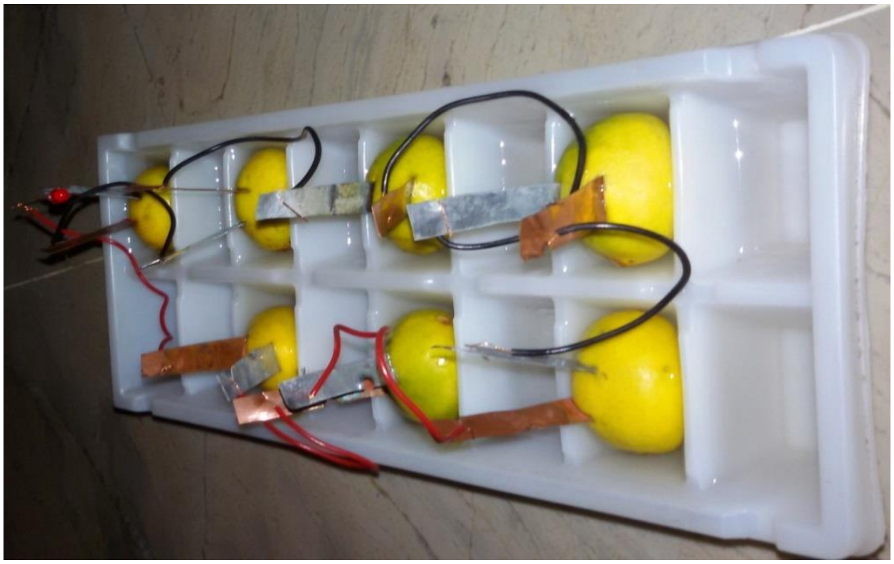

Figure 1 led bulb glow by lemon battery

Figure 2 configuration of lemon power batteres

Objectives:

1. To prepare PVC- based proton exchange membrane by taking different concentrations of the inorganic filler SiO_2 and varying the concentration of dopants (citric acid and phosphotungistic acid).

2. To study the surface morphology of the membranes by scanning electron microscopy.

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3. To find out the % water uptake and ion exchange capacity of the prepared samples.

4. To find out the tensile strength of the samples.

5. Application of prepared membranes in microbial fuel cell to find out the power density of the membrane.

EXPERIMENTAL

MATERIALS AND METHOD

Chemicals/ Glassware/ Apparatus used

- Polyvinyl chloride (PVC)
- Dimethylformamide (DMF)
- Phosphotungstic acid (PWA)
- Silica (60-120)
- Hydrochloric acid (HCl)
- Sodium hydroxide (NaOH)
- Sodium Chloride (NaCl)
- Citric acid
- N-methyl-2-pyrrolidone (NMP)
- Phenolphthalein
- Magnetic stirrer
- Petri plates
- Beaker
- Conical flask
- Burette
- Pipette

METHODOLOGY OF WORK

Membrane synthesis:

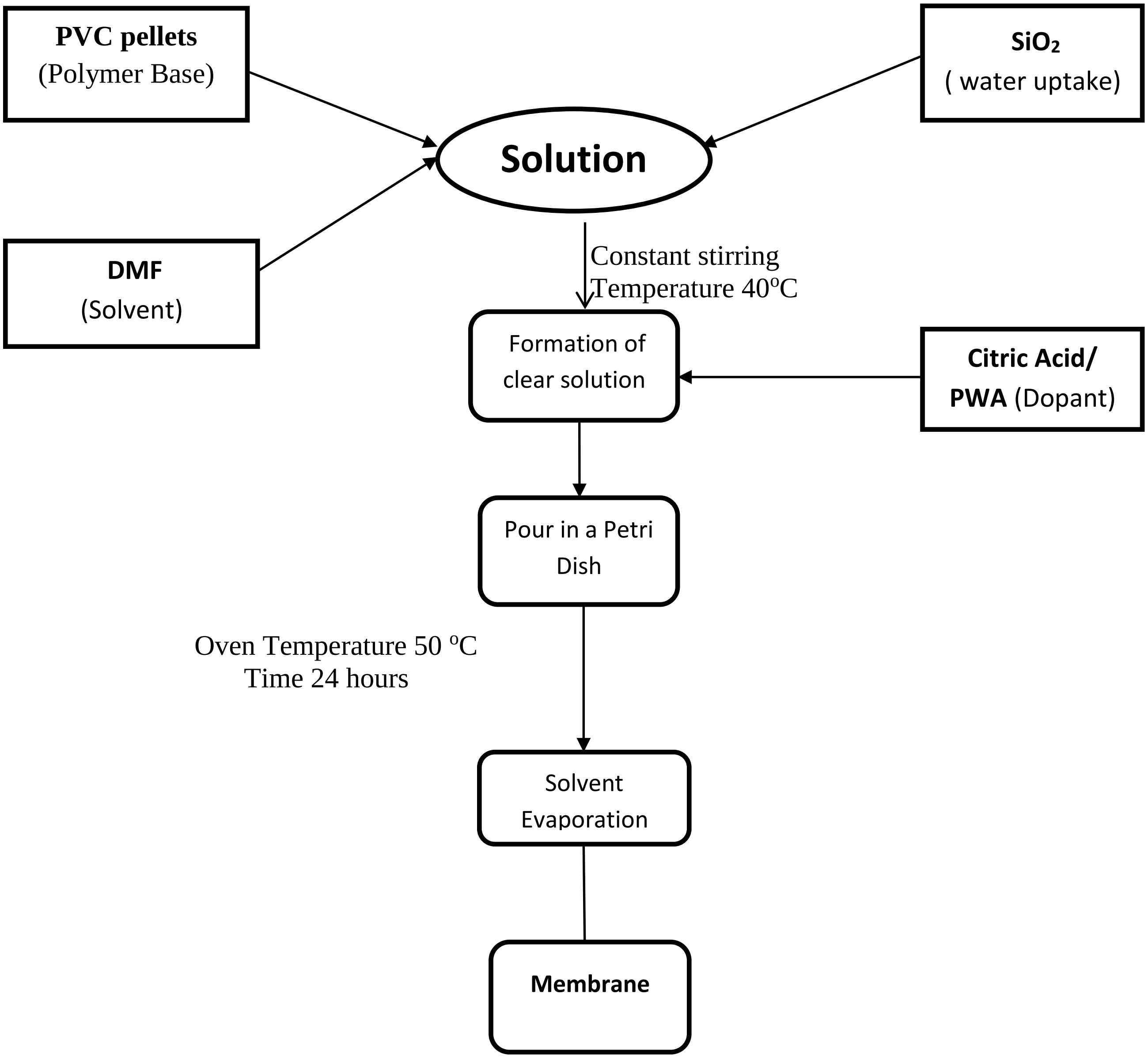
The methodology of work depicts the process and methods undertaken for the fabrication of the PVC membrane by adding various dopants in different concentration. All the above mentioned chemicals were purchased from local suppliers and used as such.

Films of pure PVC and various compositions of PVC complexed with SiO_2, citric acid and PWA were prepared in various weight percent ratios by solution cast technique using DMF as solvent. The solutions were stirred at 40 ºC for 8–10 h to get a homogenous mixture and then cast onto polypropylene dishes and allowed to evaporate solvent first at oven temperature (50 ºC) for one day followed by 4-5 days at room temperature.

The various combinations prepared are shown in Table 1:

S. No	Sample	PVC (g)	SiO_2 w/w %	Citric acid v/wt	Phosphotungstic Acid (w/w)%
1	A	2	-	-	-
2	B	2	1	-	-
3	C	2	2	-	-
4	D	2	5	-	-
5	E	2	10	-	-
6	F	2	5	10	-
7	G	2	10	10	-
8	H	2	5	20	-
9	I	2	10	20	-
10	J	2	-	-	1
11	K	2	5	-	1
12	L	2	5		2
13	M	2	5		3

Flow diagram for preparation of PEM



Membrane Characterization:

Water uptake: The dry samples of all the prepared membranes were weighed and immersed in distilled water at room temperature for 24 hours. Next day the samples were taken out and surface water was removed with absorbent paper. All the samples were again weighed to get the wet weight. The percentage of water uptake or water retention is calculated by the following equation.

Water uptake (%) = $(W_w - W_d / W_d) \times 100$

Where W_w is the weight after immersing the samples in water and W_d dry weight, respectively.

Ion Exchange Capacity: Ion exchange capacity of the prepared membranes was evaluated according to the method described by Zaidi (2003). The membranes were first of all immersed in a 1 M HCl solution (for 24 hr) to bring them to protonic form followed by washing them with distilled water to remove any excess acid and subsequently dipping the membranes in a 0.1 M NaCl solution for 24 hr. Next day this solution was titrated with 0.01 M NaOH using phenolphthalein as an indicator. The IEC was calculated using the following equation:

$$\text{IEC(mequiv/g dry membrane)} = V_{NaOH} \text{ x Conc.}_{NaOH} / w$$

where V_{NaOH} is the volume of NaOH used in the titration, Conc._{NaOH} is the concentration of Na^+ and w is the mass (g) of dry membrane.

Tensile strength: The Tensile testing of the membranes were carried out on UTM machine (Instron) on rectangular sample strips of size 50x10x31 mm ± 4mm. Strain rate for tensile measurement was taken 12mm/minute.

Scanning Electron Microscopy (SEM): The surface morphology of nanostructure of PEM film can be determined by using SEM test. in this technique highly energetic electrons (few hundred to 100KeV) emitted from tungsten cathode are focused on specimen (spot size 1mm to 5mm) the three dimensional information of specimen surface are provide by using electromagnetic condenser lenses because resolution of provided by small electrons waves are quite high .The electron beam passes through the pairs of scanning coils from the objective lenses is able to deflect the beam in both direction such as horizontal as well as vertical and scans the rectangular surface area of samples . When primary electron beam interact with the surface of sample, the electron lose their energy by repeated scattering and absorption within the interaction volume, which extend the less than 100 nm into few micrometers on their surface which depends upon the beam accelerating voltage, atomic number of specimen and specimen density. The electrons are detected by a scintillator -photomultiplier device and resulting signal is provide two dimensional intensity distribution which can be seen and saved as digital image, where as the brightness of signal depends upon secondary electrons reaching the detector which depends upon the surface (flat steep surface and edges).

Bacteria Culture

The species *Alcaligens faecalis* of bacteria was obtained from National Chemical Laboratory (NCL), Pune. The bacterium was subcultured in 250 ml of Luria Bertani (LB) broth containing (g/L in distilled water): NaCl 10; Peptone 10 and Beef extract 10. The pH was maintained within the range of 7-7.5. The bacterium was allowed to incubate for 18 hours.

System Construction: Two chamber with Membrane

The setup consisted of two ARISTO air tight plastic containers (1550 ml) with holes of 1” diameter cut in the centre of their broader face and collar inch. (ARISTAL CPVC) inserted into them. The chambers were connected by an arrangement of PVC pipe, 1 inch. O.D. and 9 inch. length (PRINCE) and Union 1 inch. (JSI). Both the membranes RO (DOW) and Ultrex CMI-7000 (MEMBRANE INTERNATIONAL INC., NJ) were inserted into the union by easy dissembling og union. Two cylindrical electrodes were used as anode and cathode and were inserted into the chamber by making required holes in the cover of the air tight containers. The electrodes were connected with the help of aluminium wire. The wires were than attached to the two electrodes of the multimeter (UNI-T®) with the help of electrical tape (STEELGRIP). All the vacant surfaces were sealed using M-Seal (PIDLITE) to make the anode chamber completely anaerobic.

Anolyte Composition

The anode compartment for both membrane and salt bridge were filled with medium containing (g/L): NaCl 10, Peptone 10, Beef Extract 10, Glucose 10%, Cysteine 0.75. When mediators were used, 100µM neutral red was added.

Catholyte Composition

The cathode compartments were filled with an equivalent amount of distilled water with electrodes dipped in them.

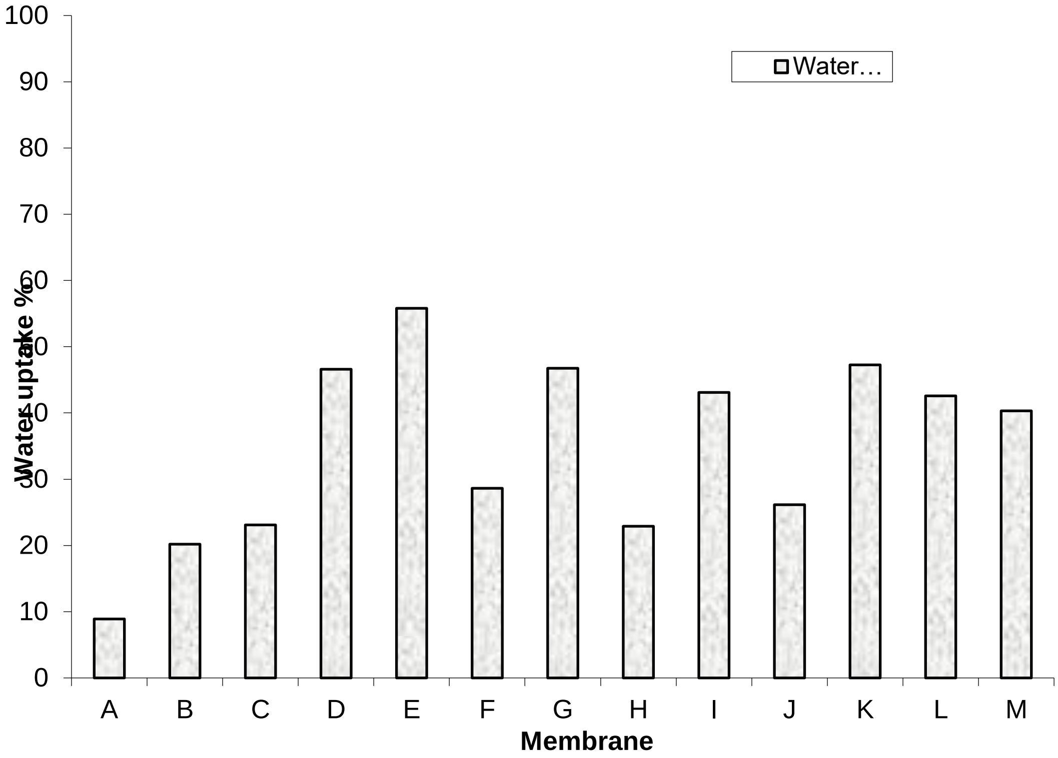
Recording of Data

Multimeter (UNI-T®) was used to get the readings at the interval of 1 hour and voltage and current were recorded in units of mV and mA respectively.

CHAPTER 3

Results and Discussion

Water uptake: All prepared membranes were tested for their water uptake capacity and the results are shown in Figure 1. All the prepared membranes were found to have higher water uptake value than the pure PVC membrane. The water uptake is observed to increase steadily with the concentration of SiO_2.

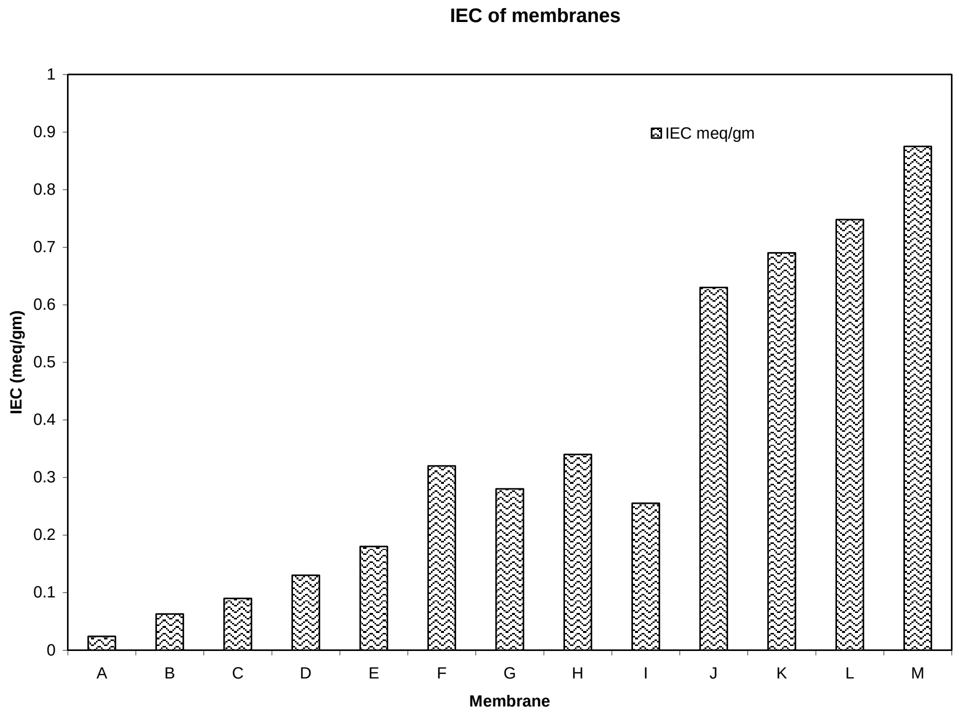


Out of four membranes where varying % of SiO_2 was introduced, 10% showed maximum water uptake of 55.8% with comparable water uptake of 46.6% at 5%. Therefore, these two concentrations were further used for preparing other membranes. This is also supported by literature where water uptake increases with increase in the % of SiO_2 [46]. Further, when citric acid was used, water uptake reduces. It shows that citric acid molecules are chemically bonded to the host polymer leading to increased crosslinking and reduction in water uptake [47]. On the addition of PWA, water uptake decreases. This is an unexpected trend in the sense that since

PWA is hydrophilic therefore water uptake should increase with increase in PWA wt.% [48,49]. Decrease of water uptake with PWA content indicates that the interaction between PVC and PWA dominates over the increase of hydrophilicity due to addition of more PWA which ultimately leads to more rigid and compact structure. The same results were obtained by another group when working on PVA/PWA/SiO2 membrane [50].

Ion Exchange Capacity:

The results of IEC are shown in Figure 2. The IEC of membranes with varying percentage of silica (B to E) are somewhat better than that of virgin membrane i.e A. This is also supported by the literature where workers showed that introduction of SiO_2 improved the ionic conductivity of membranes at room temperature [46]. The IEC values of PWA-doped-PVC system vary from 0.63 to 0.875 meq/gm. It can be seen that IEC increases almost linearly with PWA doping. Increase in IEC with PWA content is an expected trend since PWA acts as proton source here. The maximum IEC value of 0.875 meq/gm obtained with 3% PWA wt/wt but is lower than that of Nafion117 (0.98 meq/gm) [51].



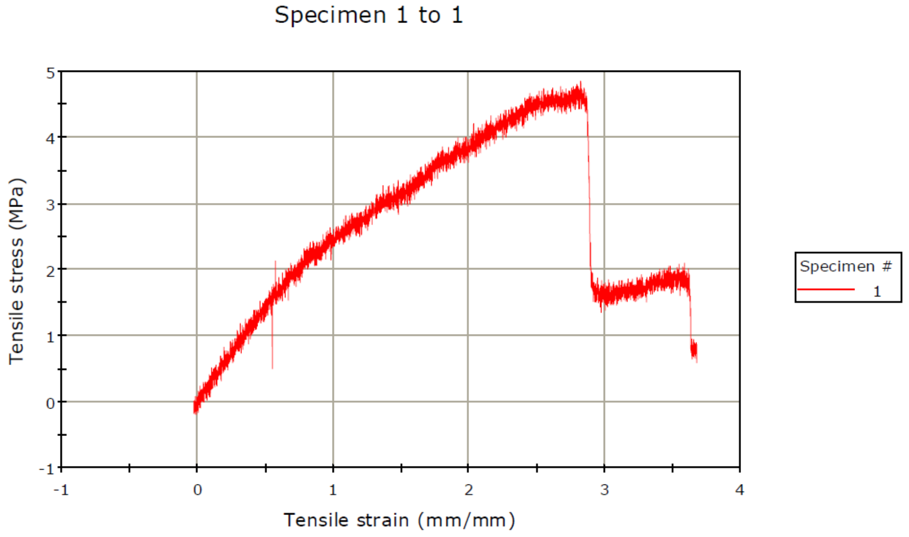
Mechanical Properties:

Tensile testing of the samples is performed in accordance with ASTM D-638. These properties are the most important indication of strength of a material. The force needed to break the specimen apart is determined, along with how much is the elongation in the material before it breaks. The ratio of stress to strain is known as tensile modulus. This is the most useful tensile data as parts should be designed to accommodate stresses to a degree well below it.

Tensile strength of PVC membrane:

DELHI COLLEGE OF ENGG.

Graph 1


Specimen 1 to 1

Results Table 1

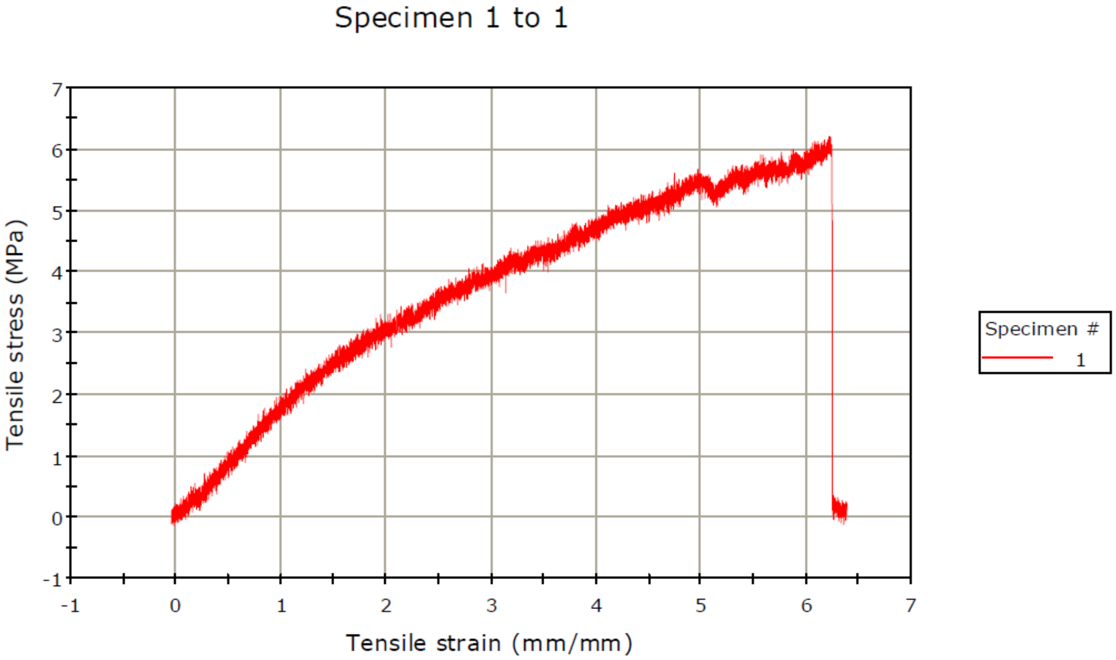
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.00873	141.17151	0.87491	50.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	185.11607

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	3.67842	185.11607	1.57484	2.90291

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	2.90291	0.03600

Graph 1



Results Table 1

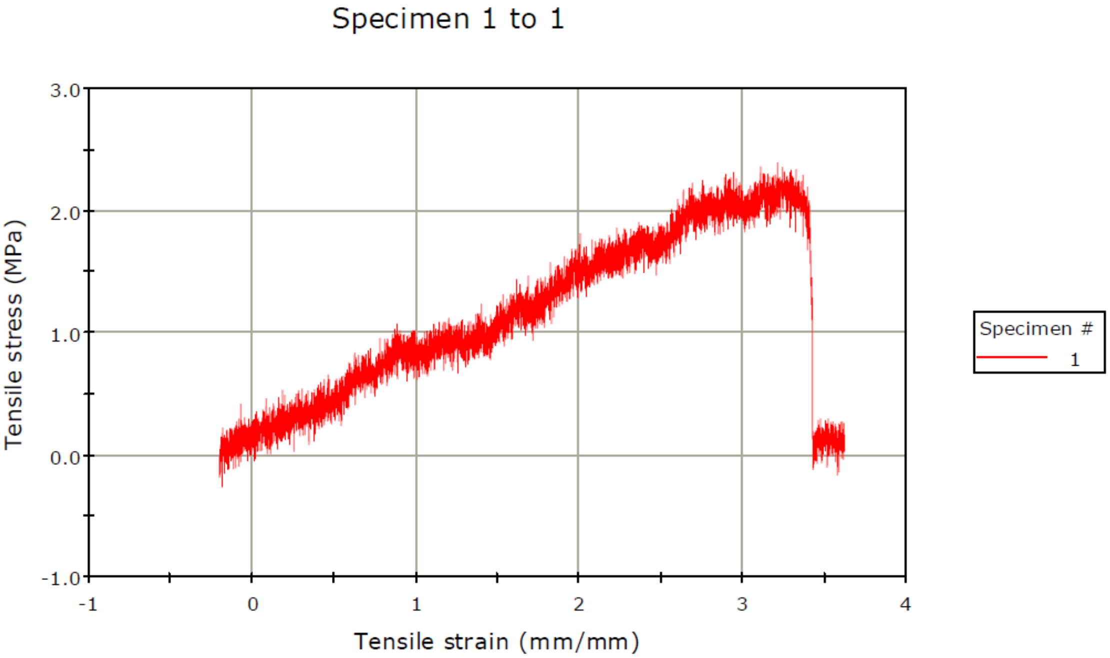
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.01116	385.20032	0.21281	62.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	398.11587

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	6.38521	398.11587	0.38305	1.73074

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	1.73074	0.03600

Graph 1



Results Table 1

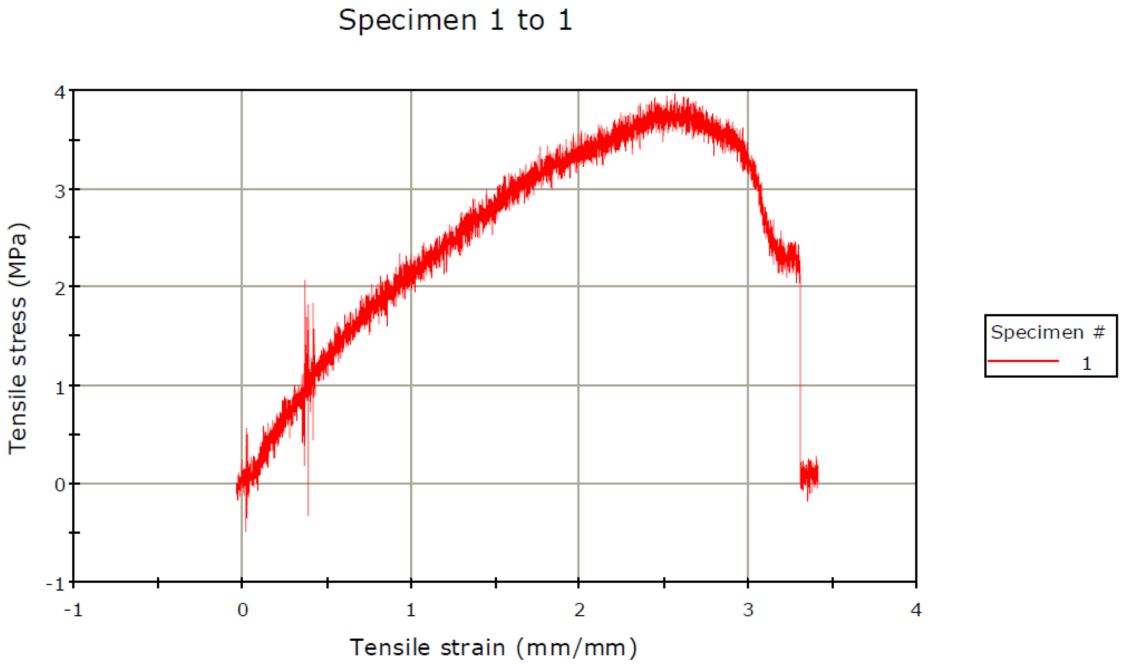
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.00430	186.27809	0.14817	58.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	221.70466

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	3.62212	221.70466	0.26671	0.93231

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	0.93231	0.03600

Graph 1



Results Table 1

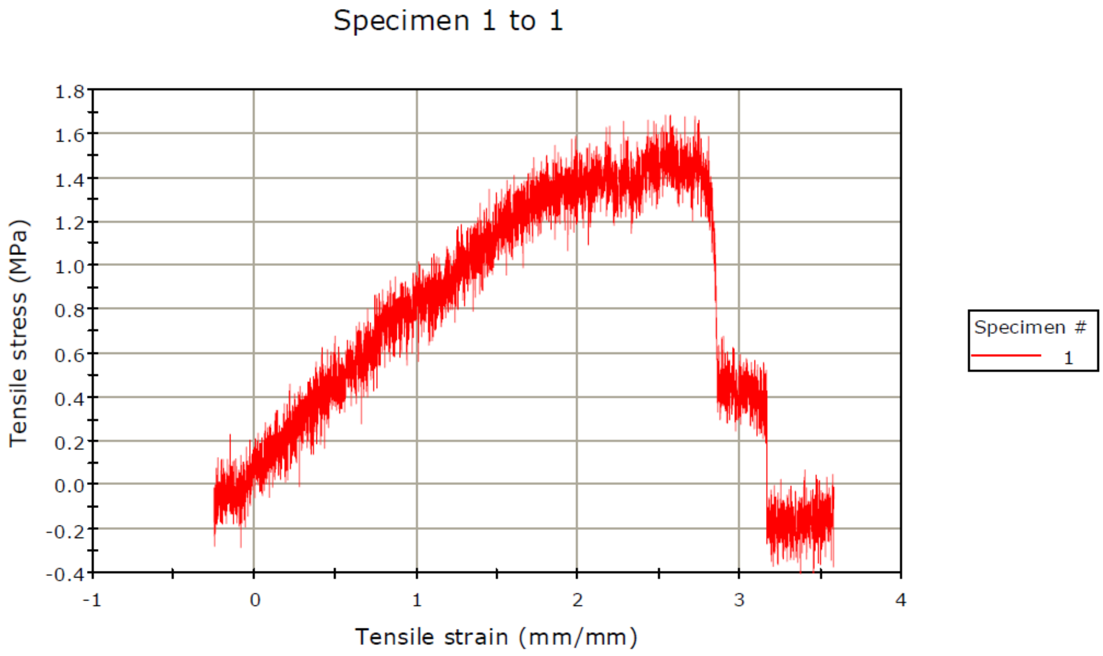
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.00713	123.07865	0.18852	48.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	165.34248

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	3.41294	165.34248	0.33934	2.60797

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	2.60797	0.03600

Graph 1



Results Table 1

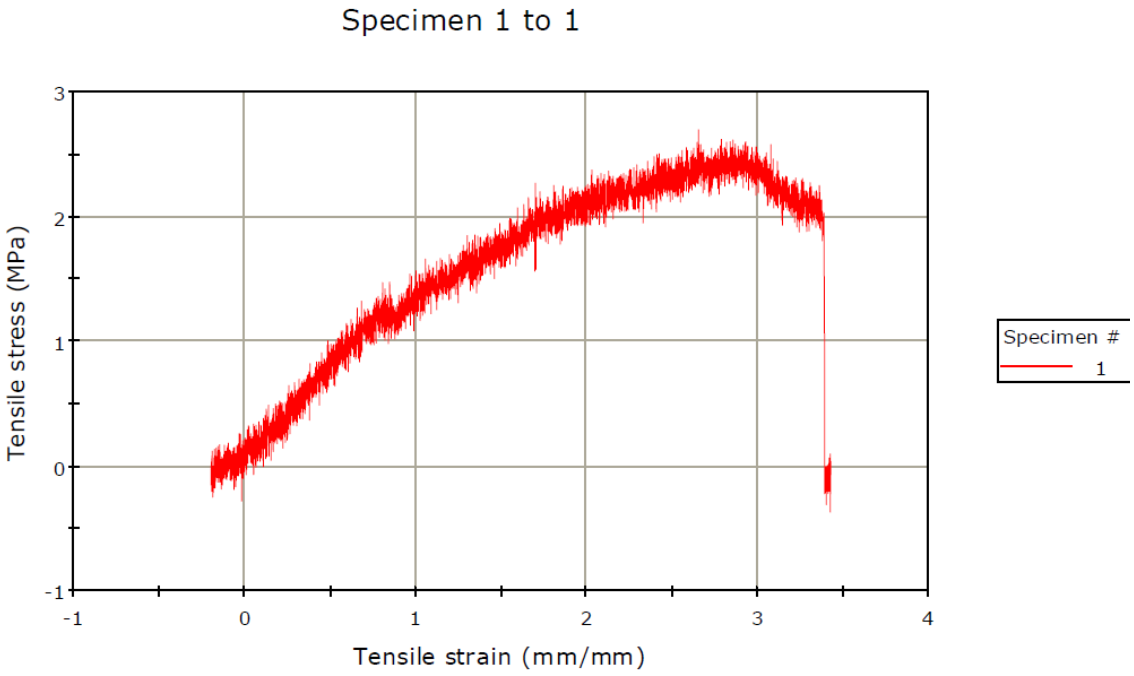
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.00303	106.69461	-0.00750	42.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	160.73528

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	3.57849	160.73528	-0.01351	0.88469

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	0.88469	0.03600

Graph 1



Results Table 1

	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.00484	140.75534	0.04140	53.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	0.15000	12.00000	1.80000	191.79809

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	3.42679	191.79809	0.07452	1.62261

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	1.62261	0.03600

SEM analysis:

SEM is carried out to study the surface morphology of the prepared membranes. As is evident from the SEM micrograph, the surface roughness of the membranes increased with increasing the SiO_2 content, Figure 9A to 9E.

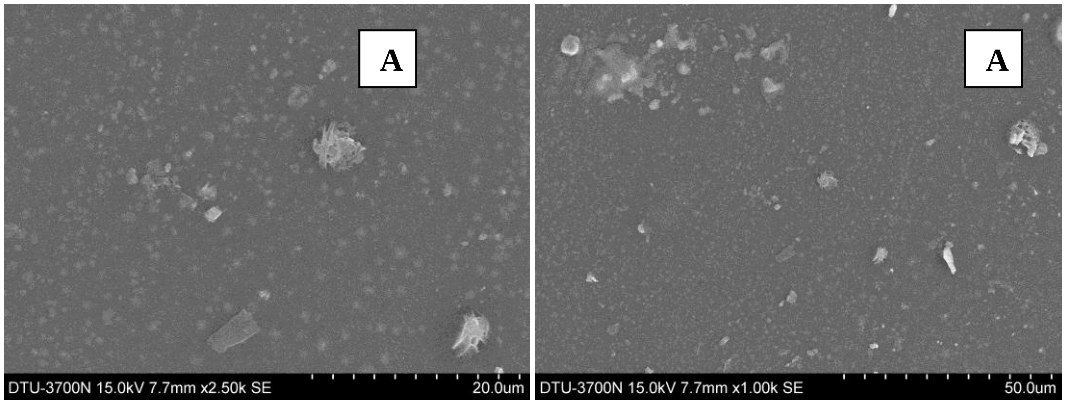


Figure 9 A: Pure PVC

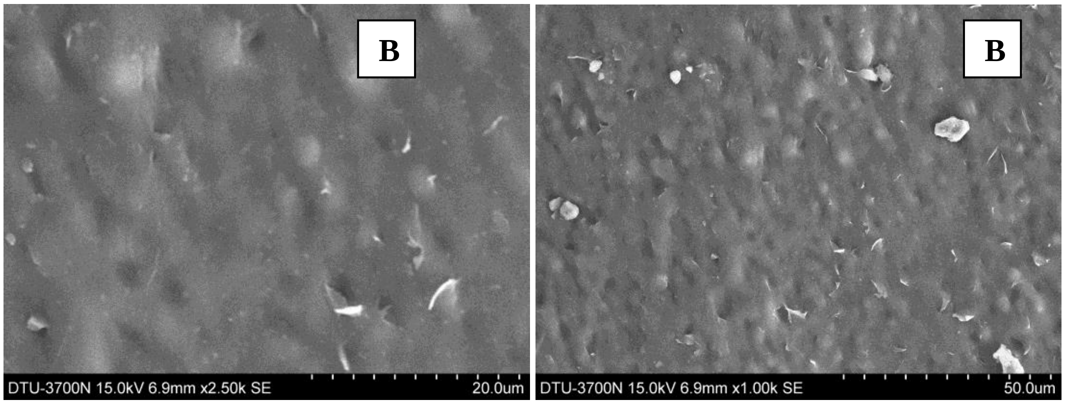


Figure 9 B: PVC + 1% SiO_2

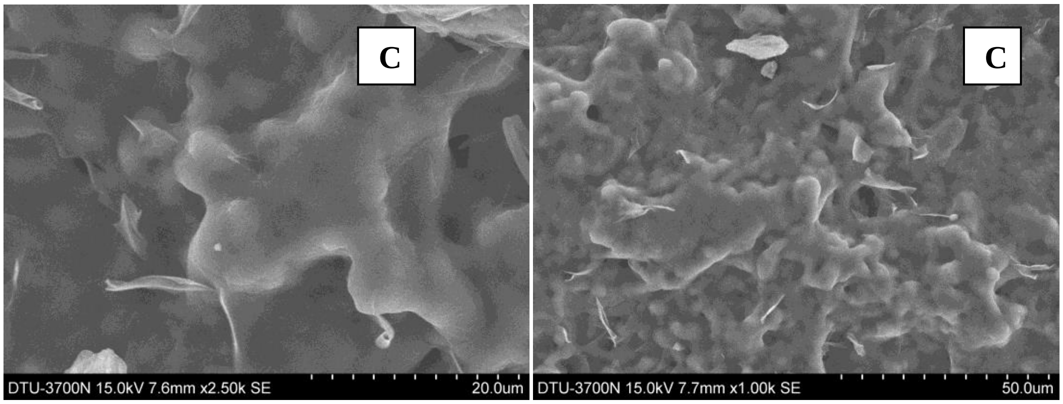


Figure 9 C: PVC + 2% SiO_2

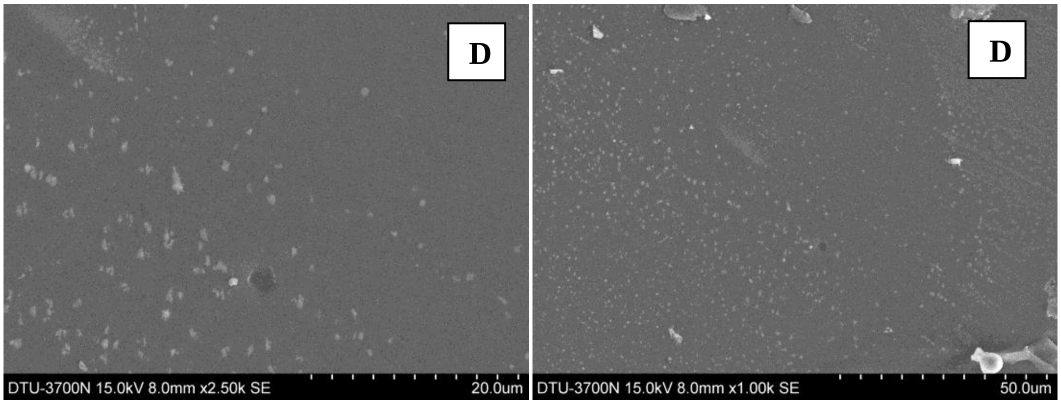


Figure 9 D: PVC + 5% SiO_2

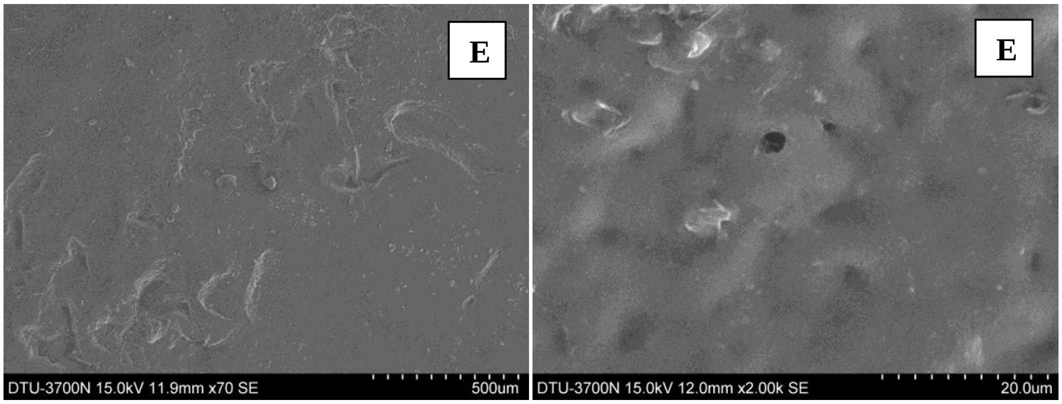
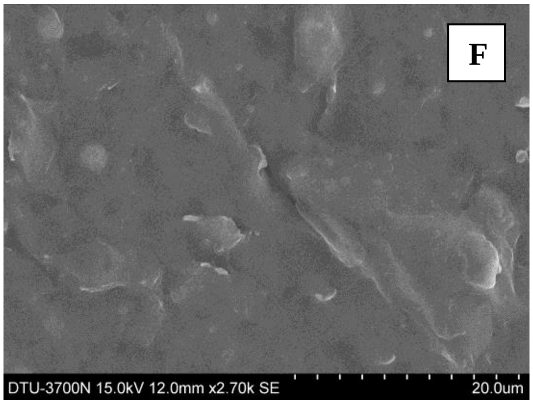


Figure 9 E: PVC + 10% SiO_2



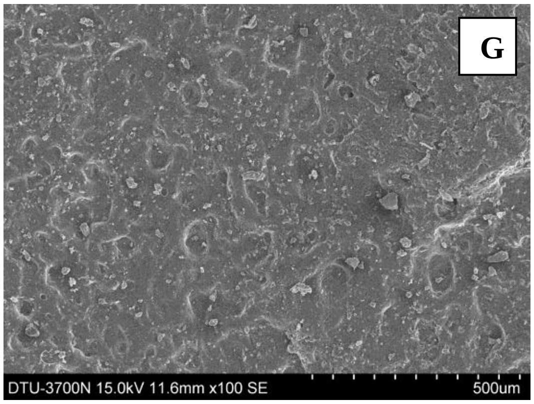


Figure 9 F: PVC + 5% SiO_2 + 1%CA

Figure 9 G: PVC + 10% SiO_2 + 1% CA

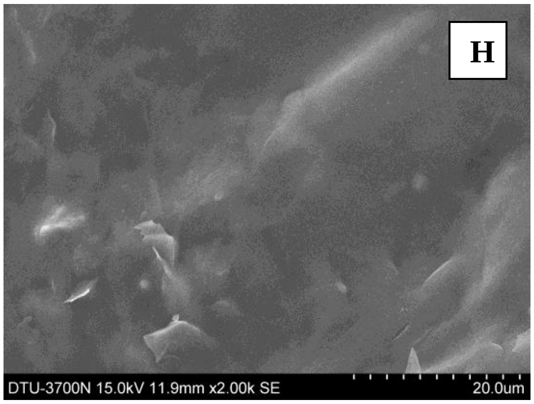


Figure 9 H: PVC + 5% SiO_2 + 2%CA

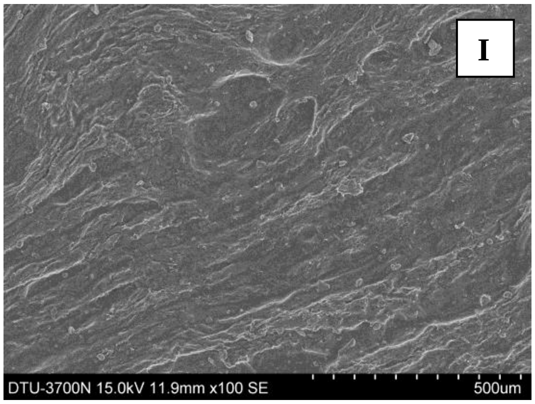


Figure 9 I: PVC + 10% SiO_2 + 2% CA

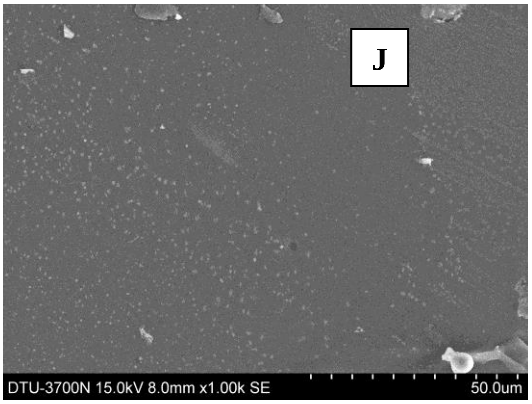


Figure 9 J: PVC + PWA

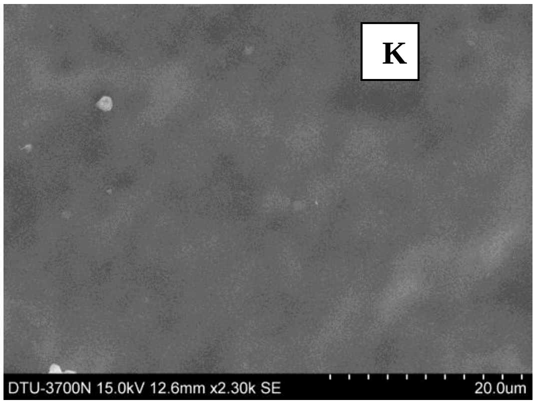


Figure 9 K: PVC + 5% SiO_2 + 1% PWA

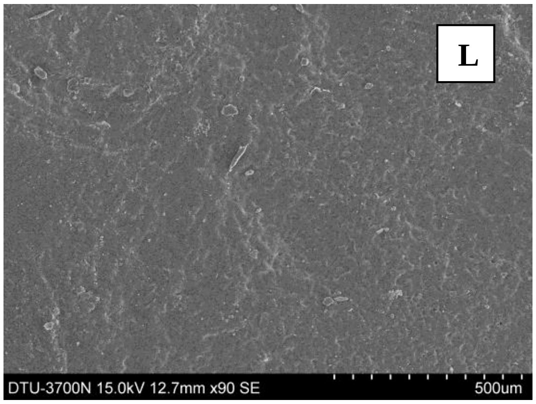


Figure 9 L: PVC + 5% SiO_2 + 2% PWA

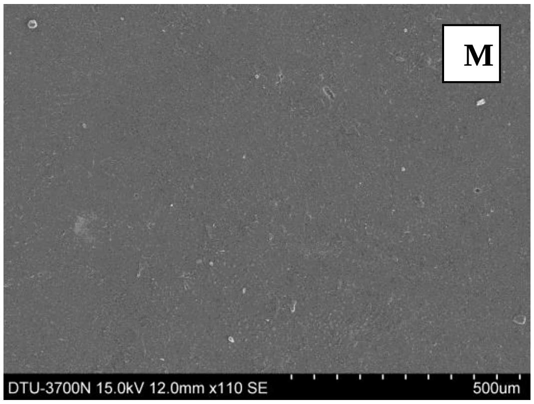


Figure 9 M: PVC + 5% SiO_2 + 3% PWA

Constructed Setup of microbial fuel cell

All the materials required for the construction of the two chamber system were assembled and setups were run with different variations. Two chamber system with a PEM is shown in figure 10 .

Figure 10: Two membrane setup with PEM configuration and no use of mediator in the medium

Calculation of Power Density

The power density for each run was calculated by using the following formula:

Power density = (V*I)/A

Where V= Observed voltage;

I= Observed current, and

A= Area of electrode dipped in the medium.

Three set of graphs were then plotted for each run ie. OCV curve, polarization curve, power density curve.

It was not possible to test the efficiency of all the prepared samples. So the membranes showing better IEC were selected for MFC set up. The results are shown below.

For membrane E

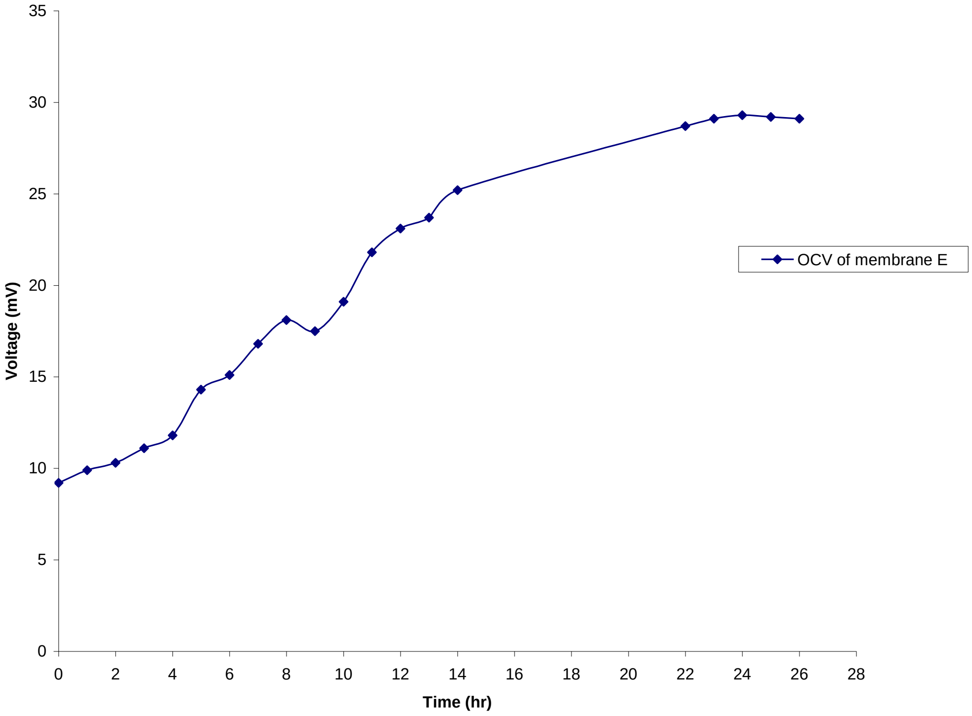


Figure 11: Open circuit voltage of E

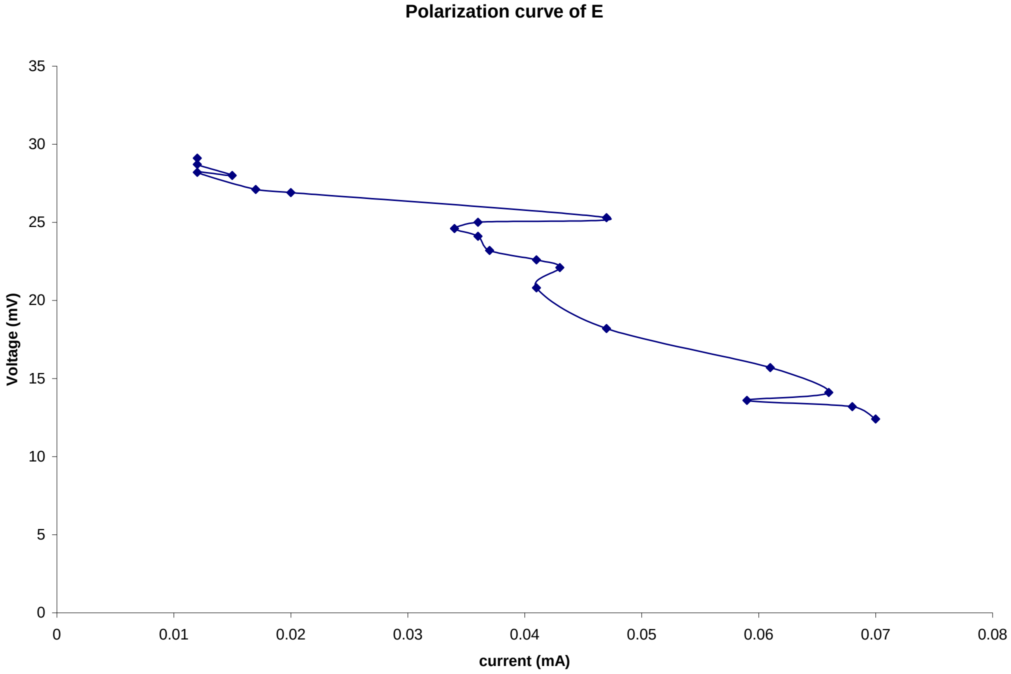


Figure 12: i-V curve of E

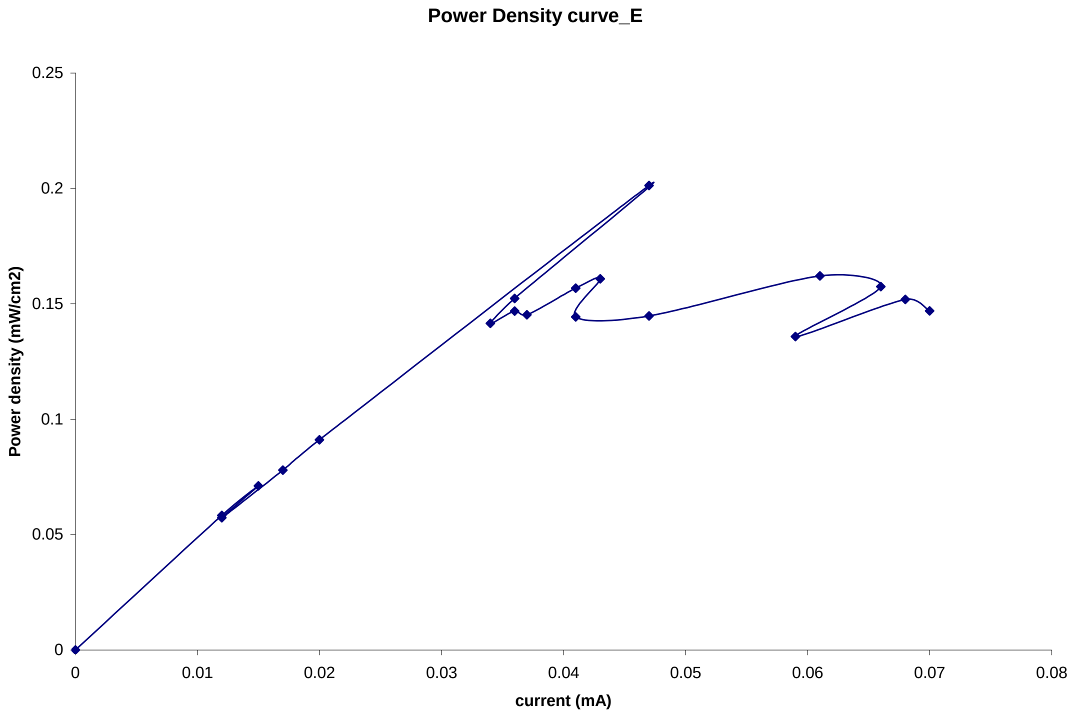


Figure 13: Power density of E

For membrane I

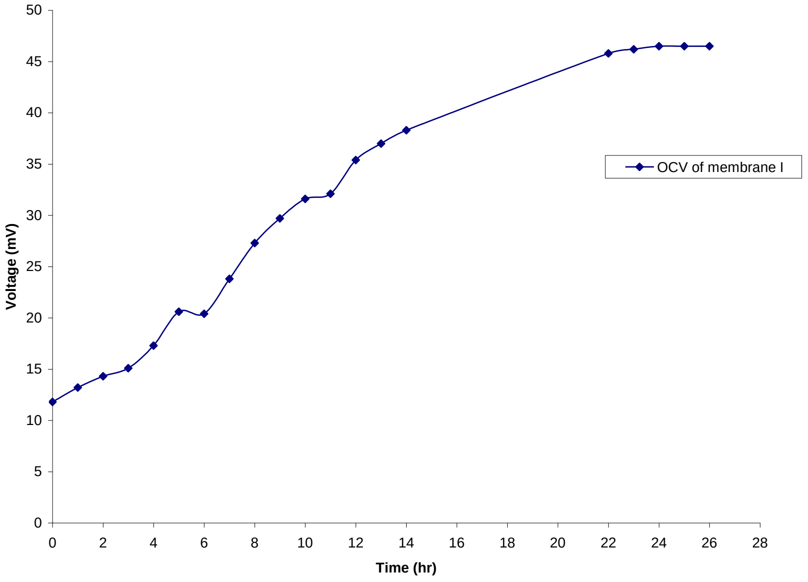


Figure 14: Open circuit voltage of I

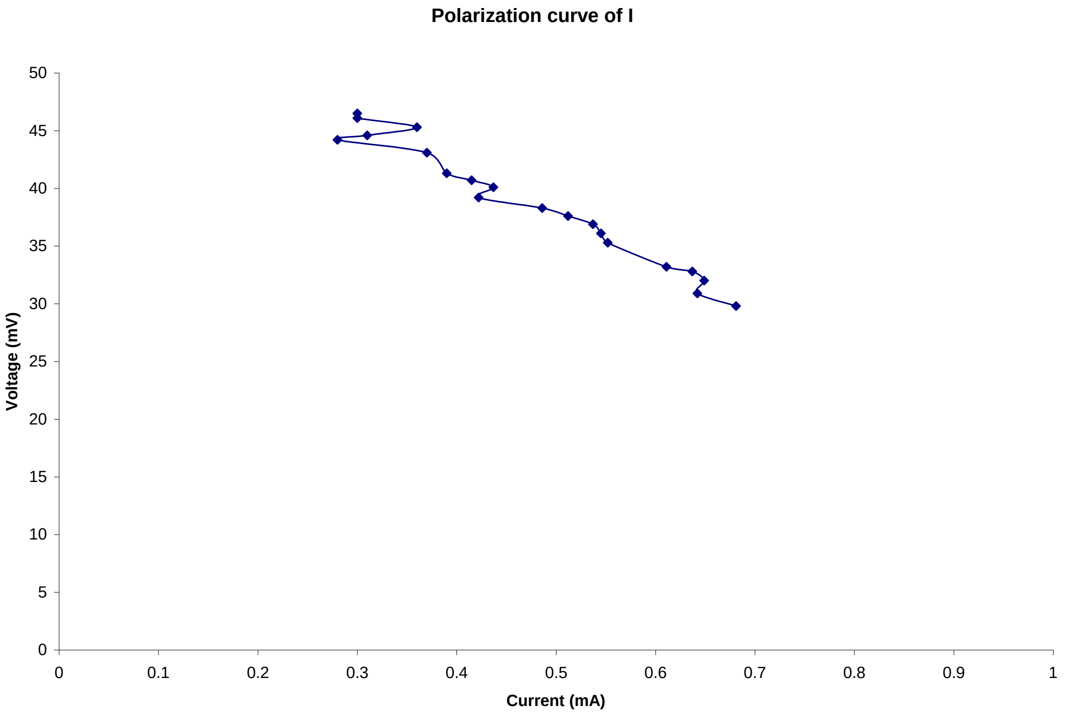


Figure 15: i-V curve of I

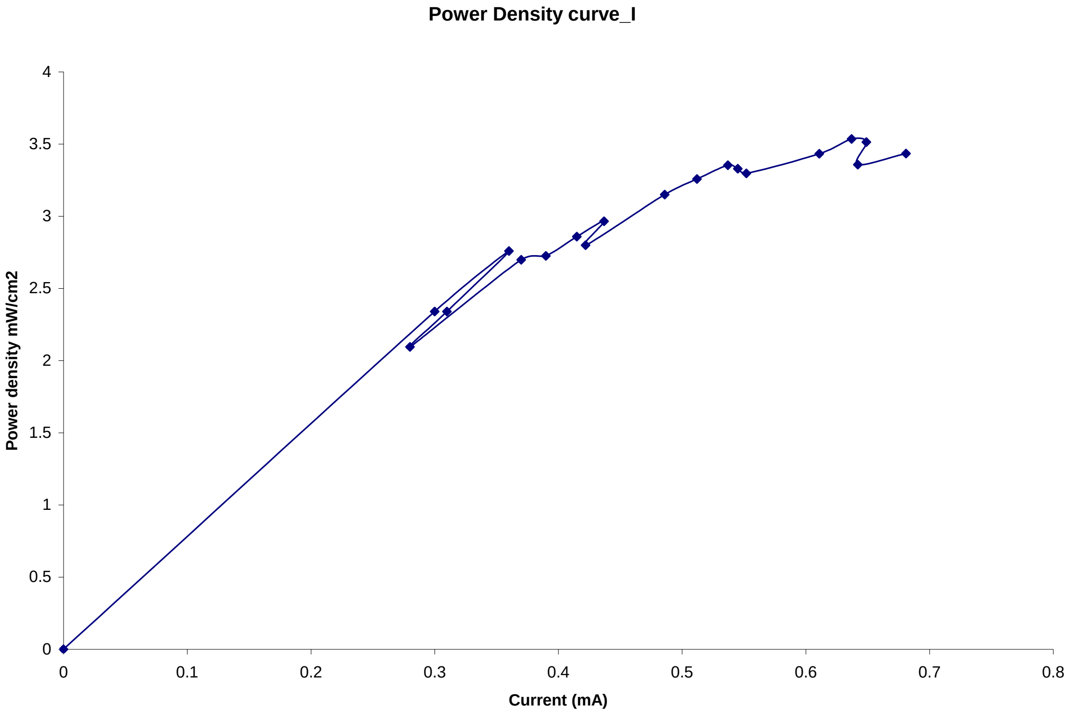


Figure 16: Power density curve of E

For membrane L

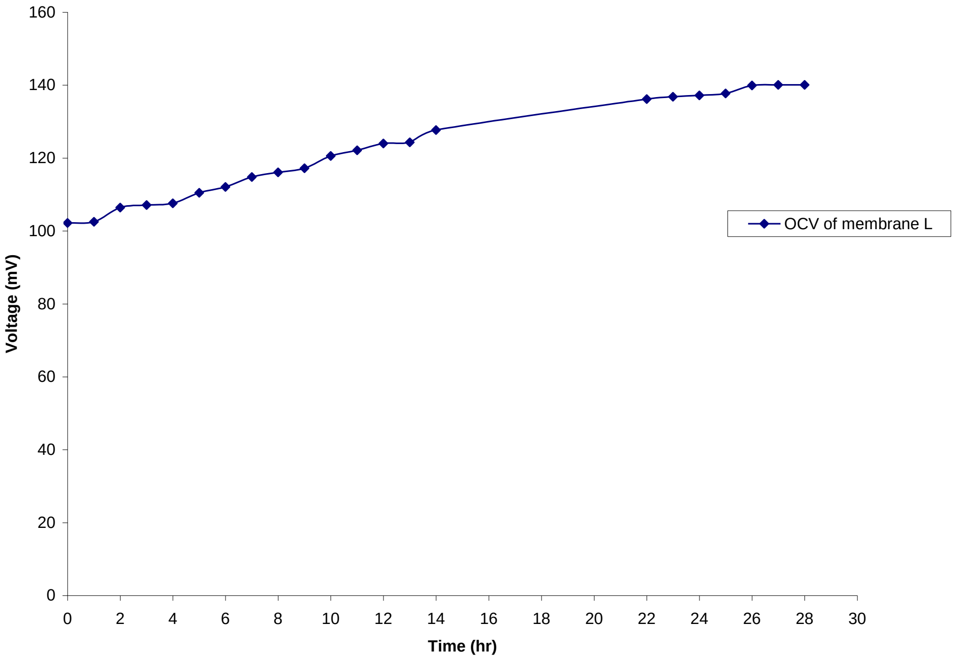


Figure 17: Open circuit voltage of L

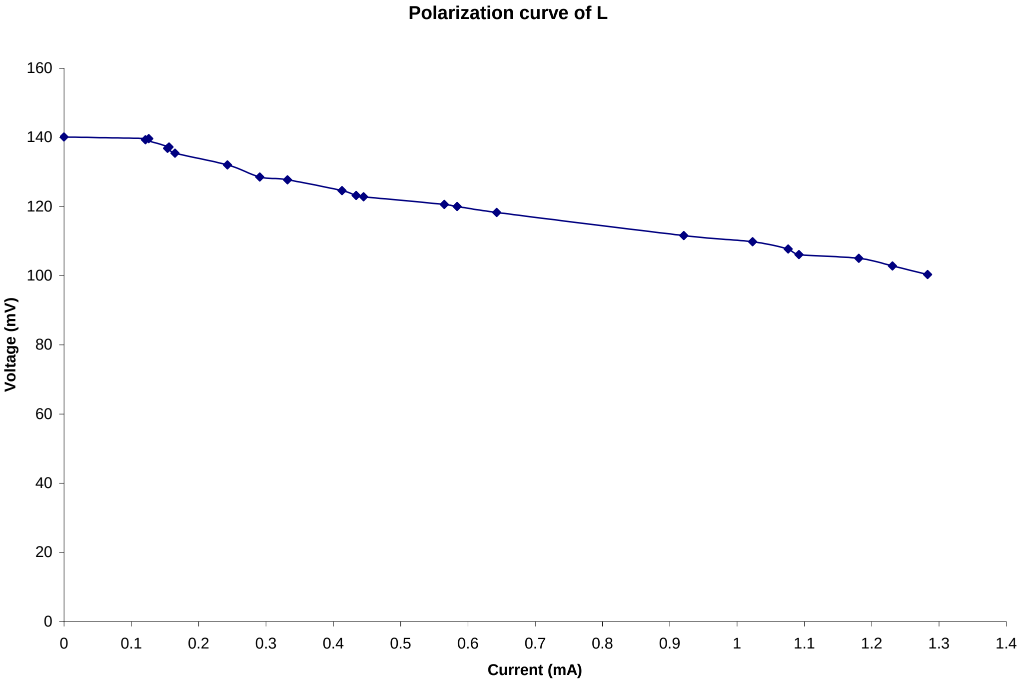


Figure 18: i-V curve of L

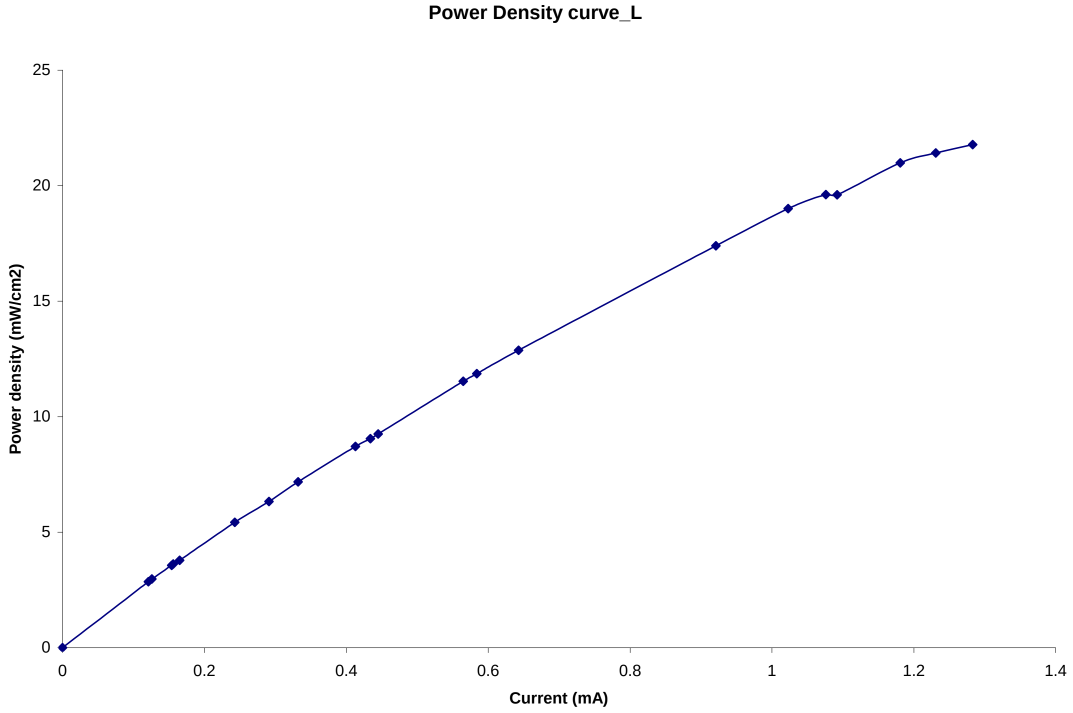


Figure 19: Power density curve of L

For membrane M

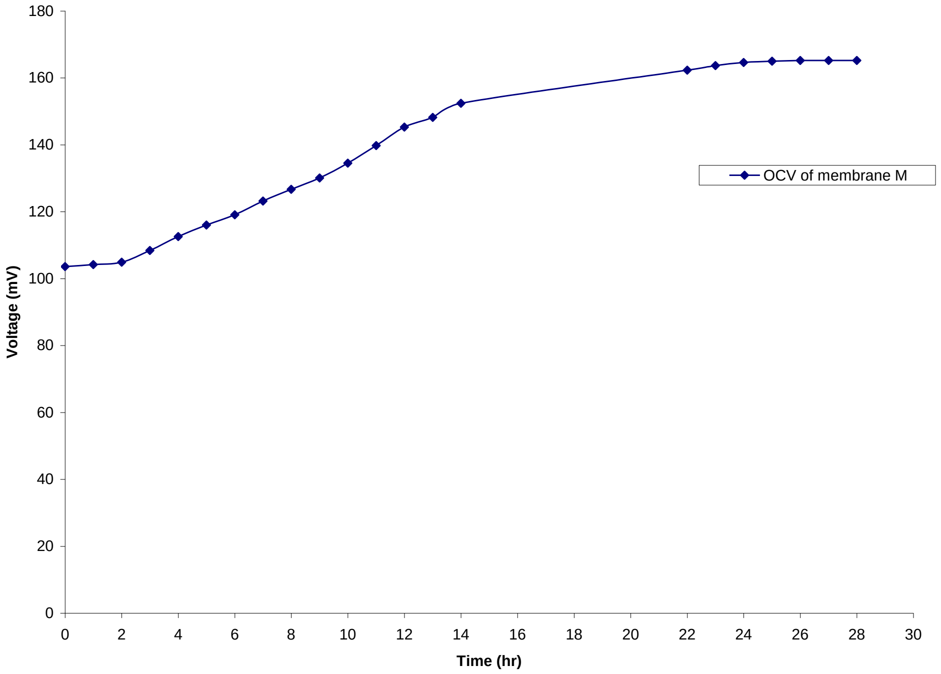


Figure 20: Open circuit voltage of M

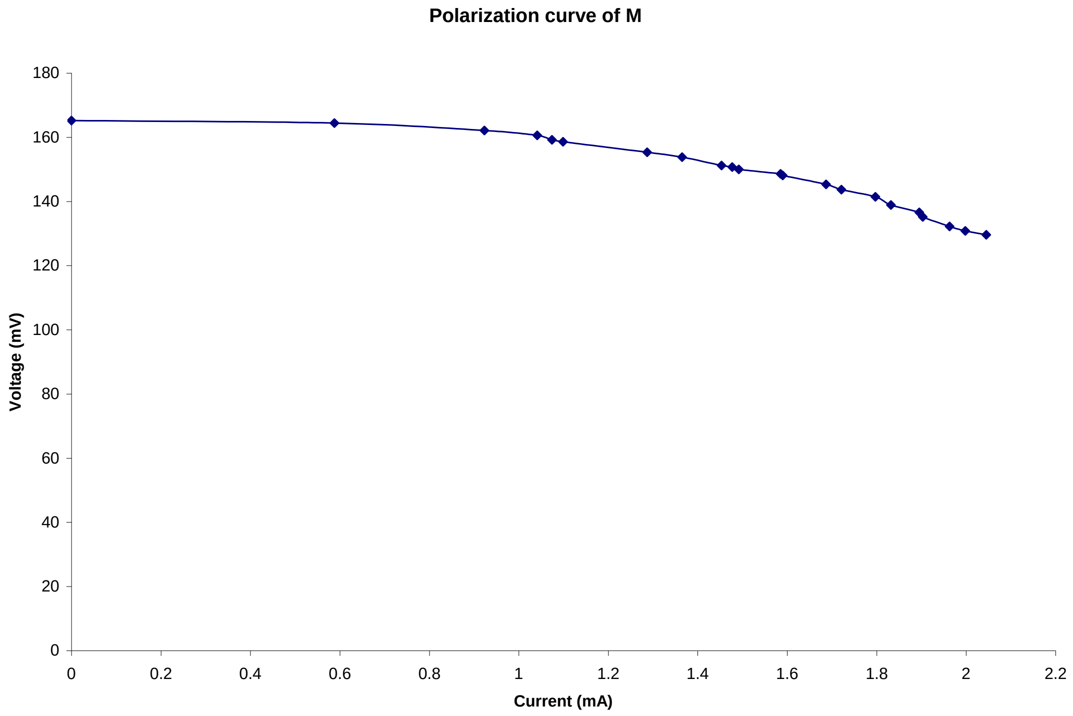


Figure 21: i-V curve of M

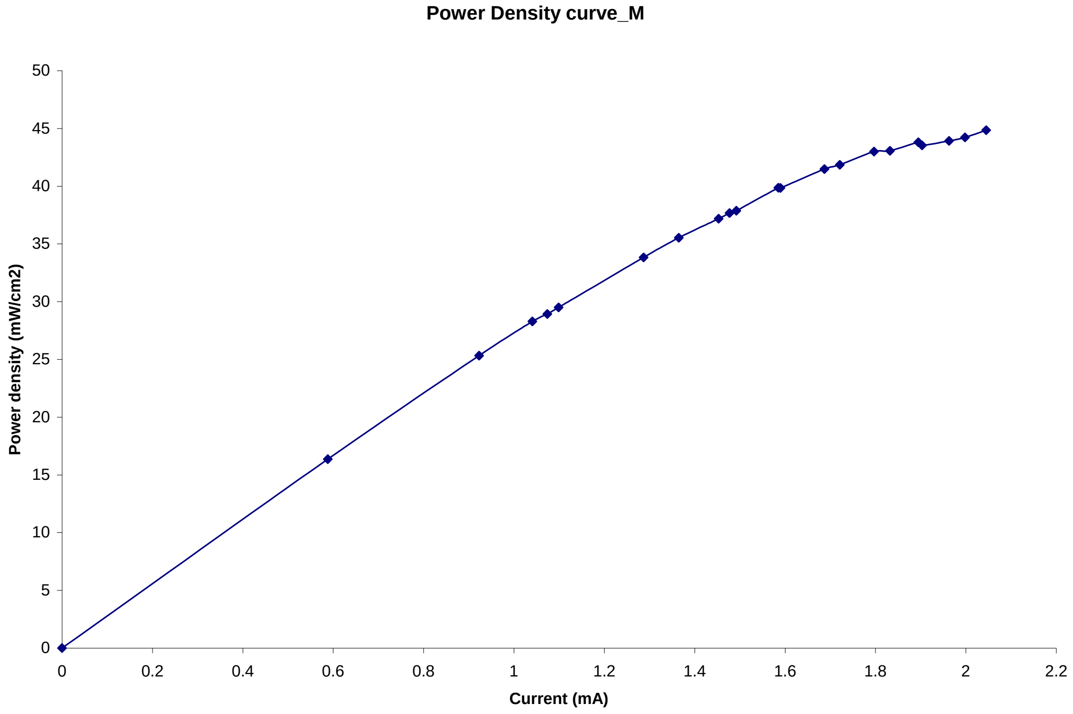


Figure 22: Power density curve of M

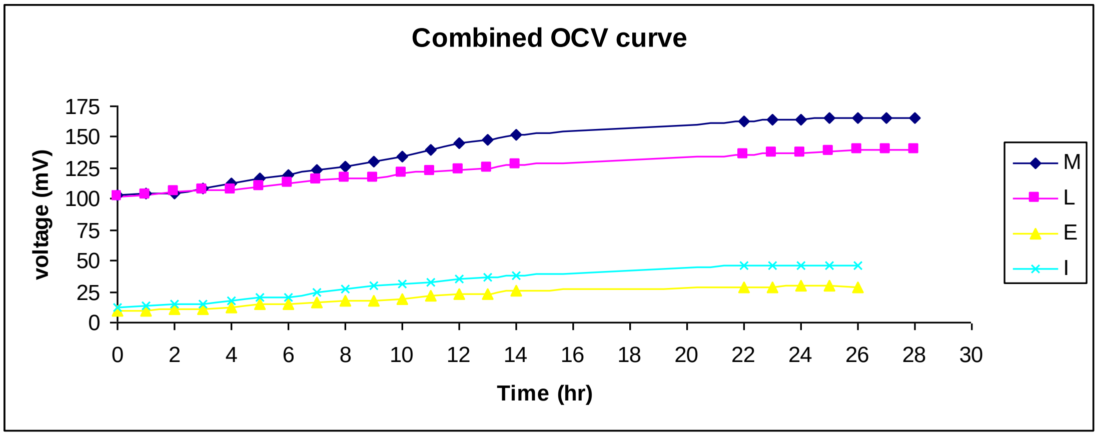


Figure 23: Combined Open circuit voltage of E, I, L and M

Nafion117 membrane have till now been used as a source of PEM connecting the anode and cathode chambers with each other in a two chamber system. Here, we have tried to compare the efficiency obtained from using newly synthesised polymer membrane with that from the regularly used Nafion membrane. From the power density curve of the MFC configurations with PEM setup (figure 13, 16, 19 and 22), it has been observed that the membranes used proves efficient as far as highest power density achieved is considered when compared with the its counterpart used and results in power output which is about 20-30 times that from the CMI-7000 membrane. It is observed that the higher amount of salt increases the net output produced and this effect can be attributed to may be the increase in conductivity due to increased flow in salt ions.

Chapter 4

Conclusion

In the present work, various membranes were prepared by using different concentrations of SiO_2 and their corresponding water uptake was studied. The inorganic nanoparticles improve the ionic conductivity of polymer electrolytes by affecting the crystallinity of the host polymer. For increasing the conductivity, citric acids and phophotungestic acid (PWA), a heteropolyacid, has been used here. The water uptake percentage and ion exchange capacity of resulting membranes was carried out by simple titration. Surface morphology was studied by SEM and tensile strength of the prepared samples was calculated. For the fuel cell usage the OCV curve, Polarization curve and the Power density curve was plotted to check the efficiency of the membranes. The power density obtained in case of these membranes showed encouraging results as proton exchange membranes. This work ultimately results into developing membranes using easily available and low cost materials resulting into cost reduction. On the basis of power density vs. time plots of the MFC configurations setup by us we conclude that some of the prepared membranes used proves very efficient when the factor of highest power density achieved is considered.

In future it can act upon the bio-waste and sludge from various sources, with many setups coupled together a significant energy can be generated which would at least be very sufficient for efficient sensing systems for checking water pollution.

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