

FABRICATION OF FLEXIBLE ELECTRODE FOR PEMFC USING INKJETPRINTING

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ABSTRACT

Polyelectrolyte Membrane Fuel cells (PEMFCs) are energy efficient alternative to combustion engines for automotive and are on the cusp of mass-production. Significant advances have been made in PEMFC system design. The membrane electrode assembly (MEA), especially the electrode is considered to be 'the heart' of a PEMFC and is designed to accommodate constraints imposed by the cost of platinum used for efficient transport of electrons, reactants and heat. Our main aim is to reduce the Platinum or Platinum group metal (PGM) loading by employing a thin coating of Platinum or PGM based catalytic layer on a thin nanostructured conductive support. The Print-Expose-Develop process developed by our group is used to fabricate the porous, conductive silver nanostructure on Nafion membrane. Higher loading of silver ($3\text{mg}/\text{cm}^2$) was used to increase the conductivity and stability of Silver nanowire network on the Nafion membrane. PEL (Poly electrolyte) treatment was used to make the Nafion membrane hydrophilic and the optimized treatment procedures for various loading were explored. Self-terminating process was used for platinum monolayer deposition on to silver nanowire structure to form a porous, electro catalytic active catalyst layer for PEMFC uses.

Contents

1	Introduction.....	7
1.1	The current state of the art PEMFC design	8
1.2	Inkjet Printing of AgNW.....	11
1.3	Nafion Membrane Structure.....	13
1.4	Self-terminating platinum electrodeposition.....	18
2	Experimental results and discussions	20
2.1	Inkjet printing of Ag nanowire network on plastic substrate.....	20
2.1.1	PEL Treatment of PET sheets.....	20
2.2	Inkjet printing of Ag nanowire network on plastic substrate with different bilayers of PEL coating	24
2.2.1	Methodology -1	24
2.2.2	Observations	25
2.2.3	Methodology-2	28
2.2.4	Observations	30
2.3	Inkjet printing of Ag nanowire network on Nafion substrate with different bilayers of PEL coating	33
2.3.1	Observations	34
2.4	Electrochemical experiments	37
2.4.1	Platinum electrodeposition on silver nanowire Setup for electrodeposition	37
2.4.2	Platinum electrodeposition using Chronoamperometry	38
2.4.3	Cyclic Voltammetry of Pt deposited Ag Nanowire Substrate.....	42
3	Conclusions	47
4	Future scope	48

Appendix A: Loading Calculations & Developer solution preparation.....	49
Appendix B: Plasma Cleaner	51
Appendix C: Poly Vinyl Alcohol coating of OHP substrate.....	52
References ...	54

Chapter 1

Introduction

The rapidly increasing population has prompted the search for alternative sources of energy generation. Conventional energy sources are non-renewable, and their increased usage has caused water, land and air pollution. Hence, it behoves researchers to look for technological advancements to develop renewable energy systems with improved energy conversion efficiencies. Contrary to the prevalent fossil fuel-based technologies, Poly Electrolyte Membrane Fuel Cell (PEMFC) technology is a promising and energy-efficient technology for use in vehicles, as well as portable and stationary power applications, which converts chemical energy to electrical energy. It causes less harm to the environment since it does not emit CO_2 , CO , SO_x or NO_x gases instead, it provides pure water as a by-product. PEMFCs use H_2 as a fuel, which has the highest calorific value among all the energy sources so far and is considered as a fuel for future. Unlike in conventional internal combustion engine, fuel cells are not limited by Carnot efficiencies; they operate at low-temperatures which is conducive for rapid start-up, have higher power density and can be used in stacks to extract high power output for different systems. However, a major bottleneck for mass-production of PEMFC systems is their cost. Given the potential which fuel cell technology has, its development as a viable energy conversion device is the need of an hour.

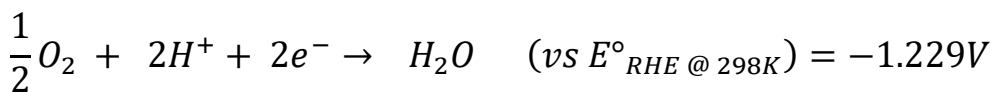
1.1 The current state of the art PEMFC design

A PEMFC is an electrochemical cell which used H_2 and O_2 as reactants. There are 2 ways to combine H_2 and O_2 , one of which is to directly combine them in the gaseous phase, where electrons are directly transferred to the molecular level, and combustion happens, which is uncontrolled, like what happens in the ICE vehicles. Unlike this, inside a PEMFC, H_2 and O_2 separately undergo oxidation and reduction respectively on different electro catalyst layers producing energy and water. Transport of protons takes place from anode to cathode through a proton exchange membrane (frequently called as Nafion membrane) fitted between anode and cathode. The electrons released upon H_2 oxidation pass through an external circuit and perform work. The reactions occurring at anode and cathode are given below.

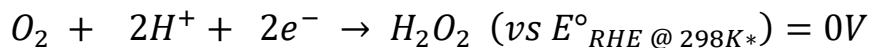
Oxidation reaction at the anode

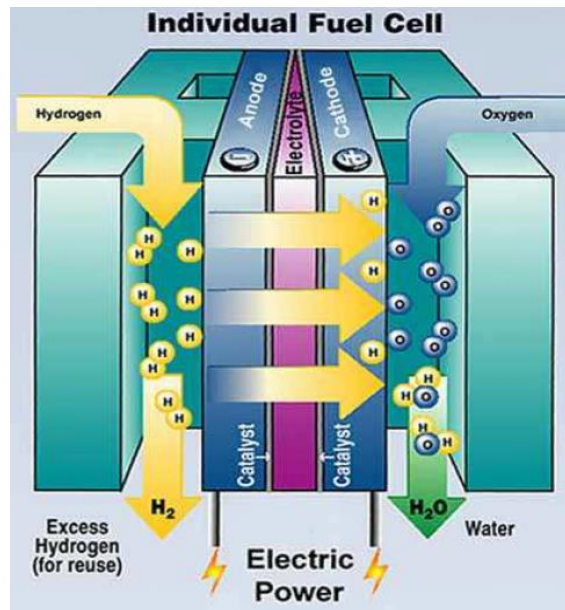


Reduction reaction at the cathode



Unwanted reduction reaction at the cathode





(1.1)

Figure 1.1: Schematic of state of the art PEMFC

Figure 1.1 shows a schematic of the PEMFC. The central part of PEMFC has anodic, and cathodic gas diffusion layers (GDL) with Nafion membrane sandwiched between the catalyst layers. This whole part is also known as the membrane electrode assembly (MEA). The gas diffusion layer (GDL) is made from carbon paper (Toray™ paper) or teflonized carbon cloth with a hydrophilic component to suck the water formed in the cathode. The GDL is responsible for transporting reactants to the reaction sites and removing water from catalyst layer. It also helps in providing the conductive pathway for electrons from the bipolar plate to the catalyst, in avoiding hotspot formation by removing the heat of reaction and supports the catalyst layer and Nafion membrane against the pressure of the inlet gaseous reactants. The thickness of the GDL is approximately 30 μm . Since the specific conductivity of the GDL material is low and as it must have sufficient conductivity for electron passage, it must be this thick. But, thicker GDL leads to higher mass transfer losses. The catalyst layer has a random network of carbon particle dispersed in a matrix, which provides a conductive pathway for electron transfer while platinum particles are dispersed on it for catalytic activity. The protonic conductivity within the catalyst layer occurs by mixing Nafion solution with the catalyst particles. Bipolar plates having channels are installed to direct the gas flows and to collect current.

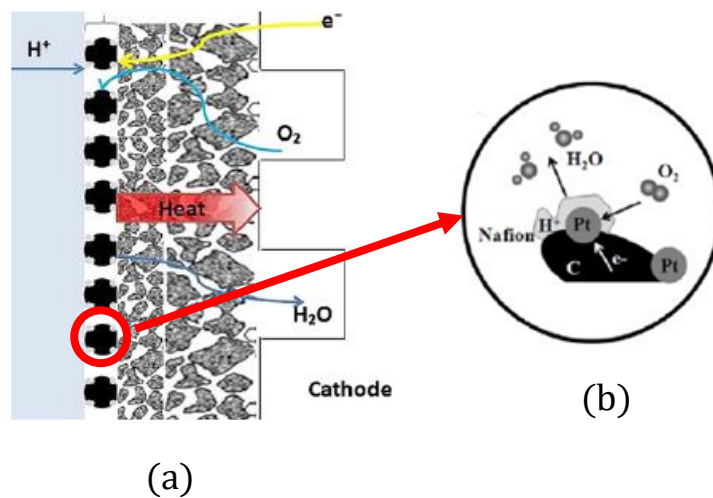


Figure 1.2: (a) Membrane electrode having triple phase boundary (b) Enlarged view of a triple phase boundary

The schematic of Membrane Electrode Assembly (MEA) is shown in Figure 1.2. The triple phase reaction between proton, oxygen and electron at the electro-catalytic site yields water as a by-product. Due to the involvement of 4 electrons in the reduction process, requiring activation and conversion of molecular oxygen to form water, cathode catalyst needs high Pt loading and overpotential. If the catalyst has poor activity towards oxygen reduction reaction, O₂ will get converted to H₂O₂ by the 2-electron reaction as shown in equation shown above, damaging the electrolyte membrane. Because of this complicated reaction requiring high overpotential and Pt is the best catalyst for this so far, the main thrust of research in PEMFC has been towards reducing the amount of Platinum used in the cathode side of PEMFC.

Main research thrust has been into developing the PEMFC with a catalyst having as minimum platinum loading as possible with efficient electrochemically active surface area to minimize costs. Research efforts over the past four decades have helped to reduce platinum loading from 10g /cm of active fuel cell area for platinum black catalysts in 1970s to 0.4g /cm of active fuel cell area for carbon based black catalysts in 2000s. But, the problem is the corrosion of carbon base under the acidic conditions in PEMFC which leads to loss of active surface area over time as support corrosion renders some of the platinum clusters deposited on this carbon base inaccessible. Because in the issued associated with these carbon base

electrodes, more research and development efforts are being focused on developing carbonless electrodes, which are thin enough with platinum loading. One such approach is to make nanostructured thin film (NSTF) electrodes. NSTF is catching attention for preparing thin catalysts, sensors or electronics in the industry as well as academia. Several groups have taken up experimental or modelling approaches to explore NSTF. One of the first attempts of experimental investigation by Ticinelli et al and Benardi et al. These NSTFs showed excellent repeatability across different batches of production, and uniformity in particle size spanning till sub-micron range. The sub-micron thickness of NSTF results in higher reaction per unit volume because the protons must travel much less distance between PEM and reactive sites on the catalyst, which becomes a crucial factor at higher current densities.

1.2 Inkjet Printing of AgNW

Inkjet printing is an attractive additive process for fabricating NSTFs. It has a drop on demand (DOD) technology, where ink droplets are ejected from a small hole in the print head, owing to pressure developed because of the electronic signal to a print head. This process offers adaptability to various substrates, high precision, excellent resolution, accuracy and small footprint. As such, inkjet printing has been studied by several groups. But, most of them use complicated ink formulation or post-synthesis steps like sintering for fabricating conductive structures. Contrary to this, inkjet printing of metal salts provides a straightforward and robust way to have controlled the synthesis of conductive metal substrates on flexible substrates like paper, PET and Nafion. This method avoids the need for expensive colloidal ink formulation or post-processing. So, **there exists considerable scope for this method to be utilized for the in-situ synthesis of silver nanostructures on different substrates, which could be used as a conductive, porous base to deposit platinum overlayers.**

Printing of the salt solution:

The '**print-expose-develop**' process, developed by our group posit a plausible mechanism for the formation of inter-connected silver nanowires, and demonstrate the percolating nature of the conductive films formed on paper. Recently, formation of conductive films on smooth polymer or paper substrates starting with silver nanowire containing pastes/inks have been reported. Silver grains generated within the photographic film after light exposure and development have also been used as seeds to form metallic

structures. However, *in situ* formation of conductive silver nanowire networks on paper has not been reported so far.



(1.3)

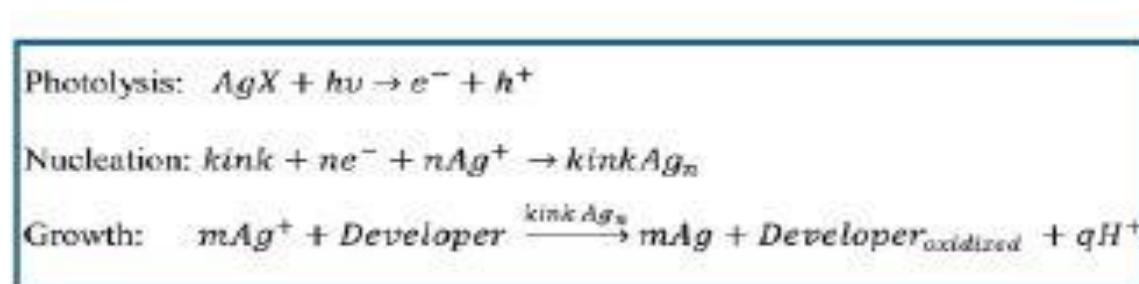
Figure 1.3 Schematic representation of ‘print-expose-develop’ process based on aqueous salt printing

DI water was used to prepare all the solutions. All chemicals used were of analytical grade or higher purity. The molar ratio of KX to AgNO₃ printed was 2:1, to ensure complete conversion to AgX on the paper. For the results reported here, a bromide: iodide :: 95:5 wt% composition was used as the halide (X) source, as addition of iodide ions enhances photosensitivity. The developer solution was pre-pared according to a standard recipe for making ID 78 (Appendix-2).

A HP Deskjet 1110 printer was used for printing the precursor salt solutions. Two separate HP 803 black ink cartridges were used for printing KX and AgNO₃ solutions. The cartridges were thoroughly cleaned by making a hole in their lids, removing the sponge holding the black ink and rinsing the reservoir in flowing tap water. Finally, DI water was filled in the reservoir and some test patterns were printed on paper until there was no evidence of black ink on paper. The black and white designs were made with Microsoft Presentation. By weighing the cartridges before and after printing DI water, the volume of solution deposited was found. To ensure spatial uniformity of the printed material, all patterns were generated using three consecutive prints of the salt solutions. After printing the desired amounts of potassium halide and silver nitrate solutions, the substrate (OHP Sheet/Nafion membrane) was kept at a distance of 50 cm under a 500 W halogen lamp (Crompton Greaves J240V 500 W R7S, 9500 Lumens) for 10 min (exposure to either sun-light on a summer afternoon in Bangalore for 1.5 h or an UV lamp (8 W, 254 nm) for 10 min also produced films with similar conductivities). Longer exposure times did not affect the measured conductivity appreciably, while shorter exposures (5 min) led to films with non-uniform conductivities and large fluctuations in measured resistance values over length scales of a few millimetres. The samples were placed in a

plastic tray containing a standard developer solution (ID-78, containing metol) for 10 min, followed by washing in a tray containing a fixer for 10 min to remove unreacted silver ions, if any (fixing does not alter the conductivity of the features). The substrate was then rinsed in water and allowed to dry under ambient conditions or dried using a hair drier.

Reaction scheme for the formation of Ag Nanowire:



(1.4)

Figure 1.4 shows the chemical reaction scheme for the formation of silver from silver halide by photographic processing.

The above figure shows a schematic of the fabrication process as well as a reaction scheme for the conversion of silver halide into silver that is adapted from literature on silver halide photography. Briefly, photoelectrons generated within the silver halide crystal react with silver ions at the kink sites (crystal defect sites on the surface) to form nuclei. The nuclei (latent images) that can be developed have at least four silver atoms. During development, the growth occurs by electron transfer between the reducing agent and silver ions. This step is catalyzed by the nuclei acting as electron reservoir (vide infra).

1.3 Nafion Membrane Structure

Nafion ionomers were developed and are produced by the E. I. DuPont Company. These materials are generated by copolymerization of a perfluorinated vinyl ether co-monomer with tetrafluoroethylene (TFE), resulting in the chemical structure given below. Equivalent weight (EW) is the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form. This is an average EW in the sense that the co-monomer sequence distribution (that is usually unknown to the investigator and largely unreported) gives a distribution in m in this formula. EW can be ascertained by acid-base titration, by analysis of atomic sulfur, and by FT-IR spectroscopy. The relationship between EW and m is

EW) 100m + 446 so that, for example, the side chains are separated by around 14 CF₂ units in a membrane of 1100 EW.

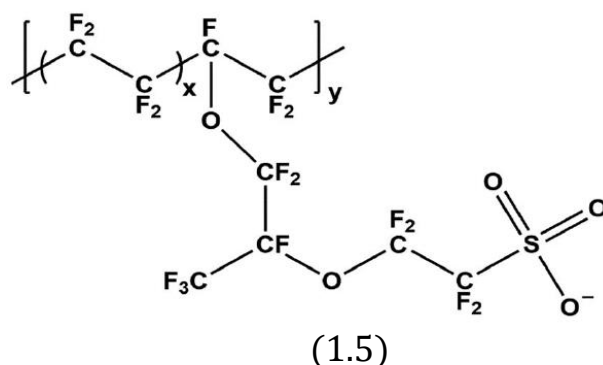


Figure 1.5: Chemical structure of Nafion membrane.

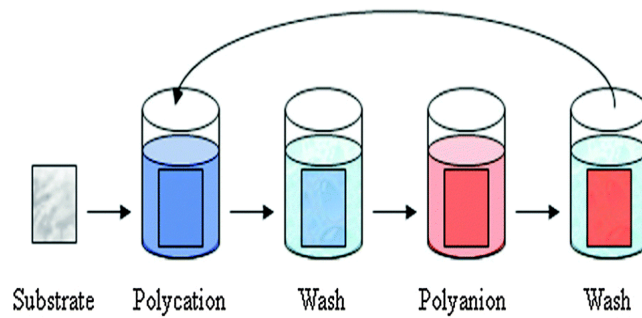
Common at the time of this writing are Nafion 117 films. The designation “117” refers to a film having 1100 EW and a nominal thickness of 0.007 in., although 115 and 112 films have also been available. Early-reported studies involved 1200 EW samples as well as special experimental varieties, some being rather thin. The equivalent weight is related to the property more often seen in the field of conventional ion exchange resins, namely the ion exchange capacity (IEC), by the equation $IEC = 1000/EW$. The mention of the molecular weight of high equivalent weight ($EW > 1000 \text{ g/mol}$) Nafion is almost absent in the literature, although the range 105-106 Da has been mentioned. As this polymer does not form true solutions, the common methods of light scattering and gel permeation chromatography cannot be used to determine molecular weight as well as the size and shape of isolated, truly dissolved molecules. Studies of the structure of this polymer in solvent (albeit not a true solution) will be mentioned in the scattering section of this review. It should be noted that Curtin et al. performed size exclusion chromatography determinations of the molecular weight distribution in Nafion aqueous dispersions after they were heated to high temperatures (230, 250, and 270 °C). Before heating, there was a high molecular weight shoulder on a bimodal distribution, due to molecular aggregates, but this shoulder disappeared upon heating, which indicated that the aggregates were disrupted. The peaks for the monomodal distribution for the heated samples were all located at molecular weights slightly higher than 105 g/mol. Also, light scattering experiments revealed that the radius of gyration had a linear dependence on the molar mass of the aggregates, which suggests that the particles are in the form of rods or ribbons, or at least some elongated structure.

Nafion ionomers are usually derived from the thermoplastic -SO₂F precursor form that can be extruded into sheets of required thickness. Strong interactions between the ionic groups are an obstacle to melt processing. This precursor does not possess the clustered morphology that will be of great concern in this article but does possess Teflon-like crystallinity which persists when the sulfonyl fluoride form is converted to, for example, the K⁺ form by reacting it with KOH in water and DMSO. Thereafter, the -SO₃H form is achieved by soaking the film in a sufficiently concentrated aqueous acid solution.

Preparation of Nafion Membrane:

Nafion membrane does not exhibit sufficient hydrophilicity (contact angle of 111.8°) for directly spreading metal salt solutions via inkjet printing. Preliminary experiments were attempted to render Nafion 211 membrane hydrophilic enough for the salt solution to spread on top of it. In the successful approach, it was pre-treated with the plasma exposure (Harrick plasma PDC-32G-2 230V). Plasma treatment activates the surface. To leverage the activated surface after plasma cleaning, the plasma-treated Nafion membrane pieces were dipped in polyelectrolyte solutions to form a hydrophilic layer. Wang et al. and Cheng et al. have also shown that the layer-by-layer (LBL) assembly of polyelectrolyte (PEL) films can improve adhesion of the metal lines fabricated by inkjet printing. These PEL films can be applied via simple methods like dip-coating, spray coating, and spin coating. The polyelectrolyte dissociates in water and produces charged species. Layer by layer deposition of polyelectrolyte multilayers (PEMs) was performed by alternatively coating plasma treated Nafion membrane with the positive and the negative polyelectrolyte. During each PEL deposition, polymer chains are adsorbed on the substrate and surface charge is reversed. Thus, an electrostatically crossed film is built up. To make the film porous enough for passage of reactants and products, 1.5M NaCl was added in both the polycationic as well as the polyanionic solution. The addition of salt helps in charge screening and leads to thicker PEL films compared to PEL films formed without any salt addition. PEL film morphology changes with different pH of the polyelectrolyte solution because of pH-dependent ionization. Application of catalyst layer for fuel cell needs sustainability in the highly acidic environment and firm adherence of the nanostructured film on the Nafion membrane. So, Polycation - [poly (diallyl dimethyl ammonium chloride)] PDDA and Polyanionic [poly (sodium styrene sulfonate)] PSS, being strong electrolyte with no pH-dependence, were chosen for coating onto plasma-treated Nafion membrane. The treated Nafion membrane is used for Pt deposition.

Layer-by-Layer (LBL) assembly of polyelectrolyte (PEL) films

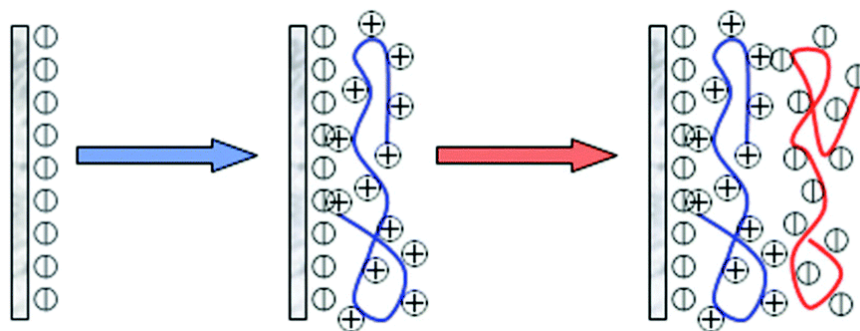


(1.6)

Figure 1.6 shows the PEL treatment process

The principle of self-assembled polyelectrolytes is a layer-by-layer assembly of oppositely charged species. Typically, alternate layers of positively and negatively charged polymers are sequentially adsorbed on the substrate from a very dilute solution to build up the interpenetrated multilayer structures. They are composed of one polycation–polyanion polyelectrolyte complex layer per dipping cycle, and that is called a bilayer.

Polyelectrolyte layers are prepared by selective absorption of compounds at solid fluid interfaces to construct organized oriented compact monolayers having a thickness ranging from about 1 to 3 nm. The molecular self-assembly process takes place as a layer-to-layer process, which is based on the spontaneous absorption of either nonionic polymers, polyanions, or polycations from diluted aqueous solutions onto surfaces that carry a functional group or a charge opposite to that of the depositing polymer. Selective absorption of these polyelectrolytes is alternated to form a bilayer assembly that leads to the formation of multilayer assemblies. **The molecules, which are typically used for constructing the first monolayer, have a terminal polar group and a non-polar functional group at either the other end of the molecule or somewhere within it.**



(1.7)

Figure 1.7 shows the formation of a bilayer after PEL coating.

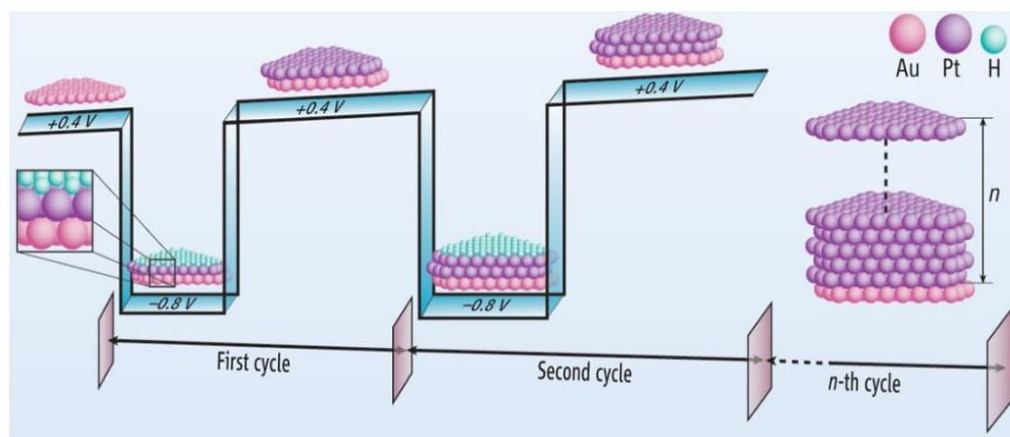
It is well known that a layer-by-layer ultrathin film can be fabricated from oppositely charged polyelectrolytes. Since Decher and his co-workers first put forward this method, referred to as self-assembly in most references, it has been widely applied in recent years in a variety of fields, including biofield, charged particles, thin metal films etc. But the electrostatic attraction was considered, especially in the recent past, not a prerequisite since the multilayer film can be fabricated from same charge carrying polymer. When the polycation poly- (diallyldimethylammonium) chloride (PDDA) is adsorbed, the contact angle in air increases; while when the polyanion poly- (styrene sulfonate) (PSS) is absorbed, the contact angle in air decreases. Because of this reason the PEL coating is always ended with PDDA coating.

For weaker electrolytes, the degree of ionization of the polymers will depend on the PH of the dipping solution & the proportion of two polymers in the final films will then depend on these PH's. Once the PEL coating is done and washed it might be expected that an excess of either polymer would be removed and final composition would always be 1:1 on a cation:anion basis. On a subsequent washing of either PDDA or PSS are immediately removed while, combined polymers form an insoluble layer. **After the first wash subsequent weight losses are quite small, showing that the PEL complex is stable.** The degree of swelling gets reduced as the polymeric ions becomes paired and there are few stretches of un-complexed polyanion/polycation. LBL films, thin multilayer films (200nm) were found to anneal from being initially rough to smooth. The annealing occurred rapidly in concentrated salt solution and very slowly in water. **So, NaCl added in PDDA and PSS apart from increasing the porous nature of the structure also increases the annealing process in the LBL films.**

If either of PSS or PDDA is present in excess it contributes to swelling of the structure so intermediate washing after is coating is necessary.

1.4 Self-terminating platinum electrodeposition

Liu et al. have shown that by stepping the potential across $-0.8\text{ V vs }V_{\text{SCCE}}^1$ and $0.4\text{ V vs }V_{\text{SCCE}}$, an atomic monolayer of platinum is formed on a gold-coated silicon wafer. The beauty of this process is that it is self-terminating in nature. In this process, after one layer of platinum deposition, hydrogen atoms get underpotentially deposited on the platinum surface which does not allow further platinum deposition unless the polarity of the working electrode is reversed to desorb that hydrogen. This process works wonderfully because when a platinum atom is deposited on substrate, a hydrogen atom also gets adsorbed on top of the platinum, leading to a Pt/H double layer which shields the deposited platinum layer from further deposition. As a result, it gives uniform platinum layers instead of 3-D islands. This process yields approximately same amount of platinum in successive cycles.



(1.8)

Figure 1.8: Self-terminating platinum electrodeposition on gold coated silicon wafer.

The schematic representation of this process is shown in (1.8) *Figure*. After successful attempt of depositing platinum on gold coated silicon wafer, Li et al. took this process to complex substrates like 3D nickel foam. They have also shown that the use of gold/ silver as a buffer layer results in a complete monolayer, unlike the case of incomplete monolayer without gold/ silver as a buffer. Getting inspired from the ability of silver on 3D substrates to form a self-terminating platinum monolayer, an attempt was made to adapt this process to silver nanowire structures developed by

¹ V_{SCCE} = Potential of sodium saturated calomel electrode

“print-expose-develop” method. This technique was adapted and Pt was deposited on AgNW coated Nafion substrate.

Chapter-2

Experimental Results and Discussions

2.1 Inkjet printing of Ag nanowire network on plastic substrate:

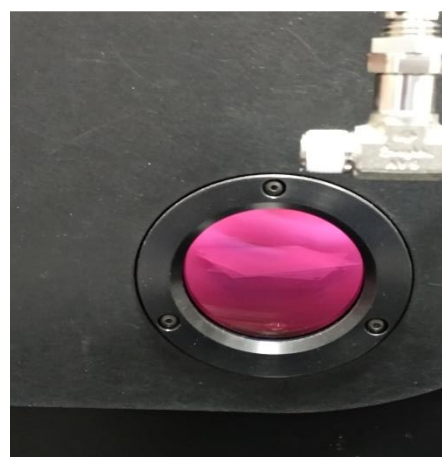
Firstly for practice purposes the plastic substrate, PET (Poly Ethylene Terephthalate) sheet of **100 microns** thickness was used to print the Ag nanowire network. The PET sheet is cut into two samples of size of 5cm x 5cm and is cleaned with Isopropyl alcohol solution.

2.1.1 PEL Treatment of PET sheets:

Then to reduce the hydrophobic nature of the PET sheet which has a dynamic contact angle of $78.7^{\circ} \pm 1.6^{\circ}$ to make them amenable for printing. The samples are first subjected to Plasma cleaning which removes all the organic matter from the surface of the samples, it also leaves a free radical on the surface to increase the bond ability of the surface. The substrates should not be subjected to plasma treatment for more than 4-6 minutes. This reduces the contact angle to less than 10° . But, since this effect is temporary one the samples should be immediately immersed in PDDA solution.



(2.1)



(2.2)

Fig 2.1 & 2.2 shows the plasma treatment of the PET substrates.

Now, to compliment the temporary effect of plasma cleaning, the samples are subjected to polyelectrolyte coating which roughens the surface and gives a reduce contact angle to the PET sheet whose effect is long lasting.

The process used is Layer-by-layer assembly of PEL film with polycation- [poly(diallyl dimethyl ammonium chloride)] PDDA and polyanionic [poly(sodiumstyrene sulfonate)] PSS. Polycation - [poly(diallyl-dimethyl ammonium chloride)] PDDA (M.Wt. - 100,000 – 200,000), 20 wt. % in water and polyanion [poly(sodium styrene sulfonate)] PSS (M.Wt. – 70,000) powder were procured from Sigma Aldrich. Sodium chloride solution of 1.5 N in water was used to dissolve the polymer solution. A 1g of PDDA solution and 2 g of PSS powder was diluted in 100 mL of 1.5 N NaCl solution to prepare the polycationic coating solution and polyanionic solution respectively. The PE sheet was treated with a cleaning solution which is a mixture of isopropyl alcohol and 1 N KOH (60:40), for 10 min and washed in DI water, PDDA and PSS were deposited alternatively onto polyester sheets with a polycationic layer on the top surface making a total of 5 bilayers.



(2.3)

Fig 2.3- Spreading of drop across the substrate was compared by dropcasting 5 μ L drop of water onto an untreated PEL sheet and PEL coated OHP sheet.

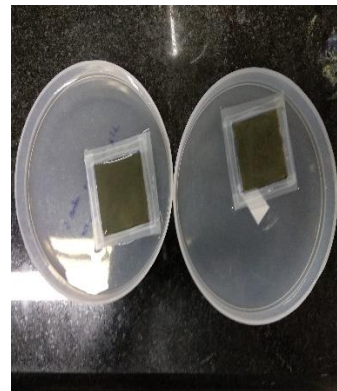
Now, after the completion of Layer-by-Layer assembly of PEL coating, the substrate has become amenable for printing. Using the inkjet printing process and with the calculated loading of 2.2 μ L/cm² & with concentrations of 2M of AgNO₃ of 2ml and 0.68g & 4M of KX(95%- KBr and 5%- KI) of 2ml and 0.068g of KI and 0.912g of KBr. The printing process was started. The pattern in which the printing was done is **KKKKAAAAA**KK a total of 6 KX print and 6 AgNO₃ print. The continuous 4K's is to increase the conductivity of the formed conductive AgX nanostructure. After the printing the samples are exposed in halogen lamp to initiate Ag nucleation and reduction for 10 minutes. After that the samples are kept in a developing solution ID-78(Phenidone Developer) overnight for complete reduction of AgX to porous, conductive Ag nanostructure.



(2.4)



(2.5)



(2.6)

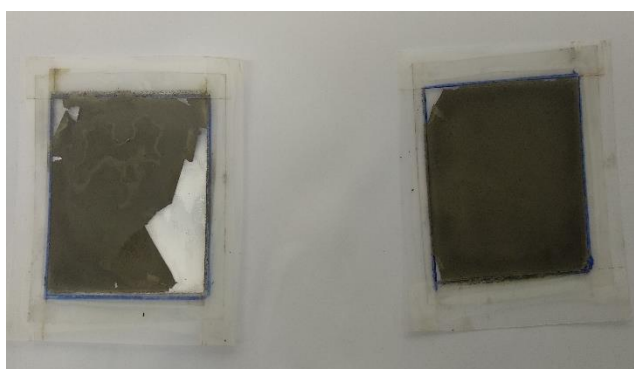
Fig 2.4, 2.5 & 2.6 shows the Print, Expose and Develop process of inkjet printing of nanostructure respectively.

After the overnight development the samples are washed with DI water to remove the residues of the developer and kept in DI water for about 3-4 hours and it is then dried completely by keeping it in the laminar hood. A small strip was cut out of the samples and subjected to electrical resistivity measurement using four probe point method.

S.No	Sample	Resistance(Ω)
1	S01	0.2
2	S02	0.1

(2.1)

Table 2.1- Resistance values of the samples



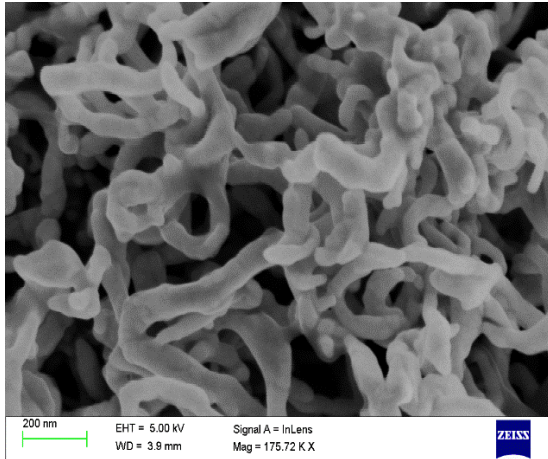
(2.7)

Fig 2.7- The dried conductive nanowire substrate is shown

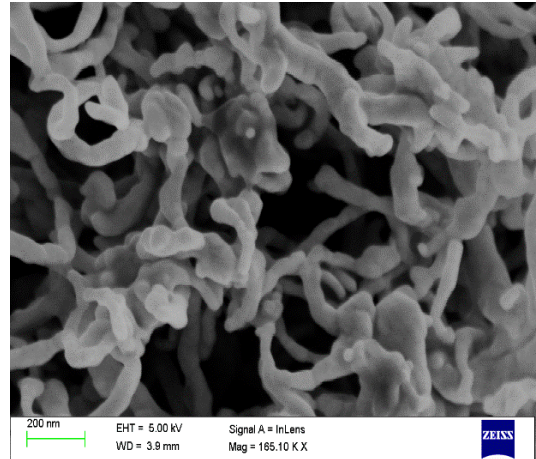
Inference:

Since, the sample (1) on the left side of Fig 2.7 is shown to have an uneven and broken conductive path it has an increased resistance of 0.2 ohms. And, the one on the right has a more even and conductive path. This sample is chosen for SEM characterization.

2.1.2 Surface Characterization:



(2.8)



(2.9)

Fig 2.8 & 2.9 The FESEM image of the developed substrate shows a uniform covering of silver nanowire network on PEL coated PE sheet respectively.

Since, to characterize a material as a nanomaterial atleast one dimension should be less than 100nm. It can be seen from the FESEM image that all the nanowire network formed is less than 100nm.

2.2 Inkjet printing of Ag nanowire network on plastic substrate with different bilayers of PEL coating:

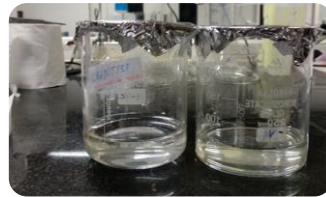
2.2.1 Methodology -1

Pre-Processing (Bilayer Treatment):

In this experiment different bilayer coatings starting from 1 to 5 bilayers with varied loadings of 1mg, 2mg & 3mg of Ag each consisting of 2 samples is prepared.



(2.10)



(2.11)



(2.12)

Fig 2.10, 2.11 & 2.12 shows the PEL treatment process, with plasma cleaning, bilayer treatment, Shaking Incubator respectively.

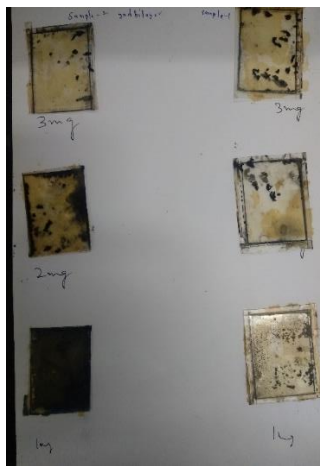
Starting with the plasma cleaning process the samples are proceeded with PEL treatment for bilayer coating and the treated samples are left in the shaker for 10 minutes. These steps are continued on for all 35 samples of OHP sheet (7 samples per batch equating to 5 batches i.e. 5 bilayers). Now to continue on the treated samples are struck on an OHP sheet and the printing process is proceeded with different Ag loading starting from 1mg-3mg. Loading calculation is attached in Appendix A.

The Print-Expose-Develop Process is continued on. And the findings are reported below.

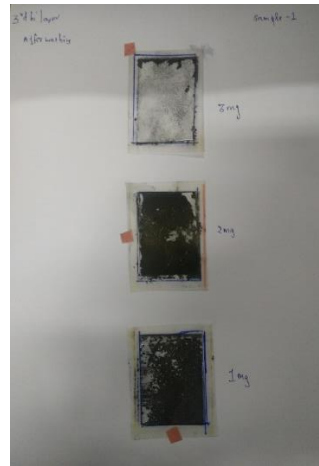
After Print-Expose-Develop Process:



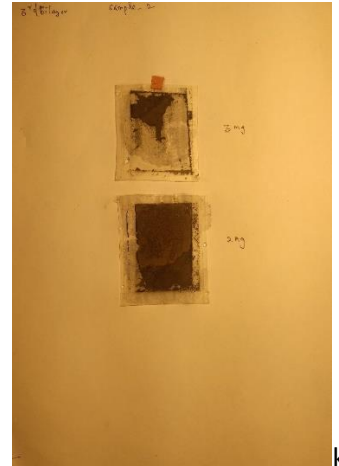
(2.13)



(2.14)



(2.15)



(2.16)

Fig 2.13, 1st Bilayer with 1mg and 2mg with 2 samples each. 2.14 2nd Bilayer with 1mg, 2mg & 3mg with 2 samples each. 2.15, 2.16 3rd Bilayer with 1mg, 2mg, 3mg respectively.

From, the above figures it can be seen that there is no uniform conductive structure is formed on the plastic substrate. With the assumption that the PEL coating has not been applied uniformly, the printing process was stopped. And the samples are characterised further to find the cause of loss in uniformity.

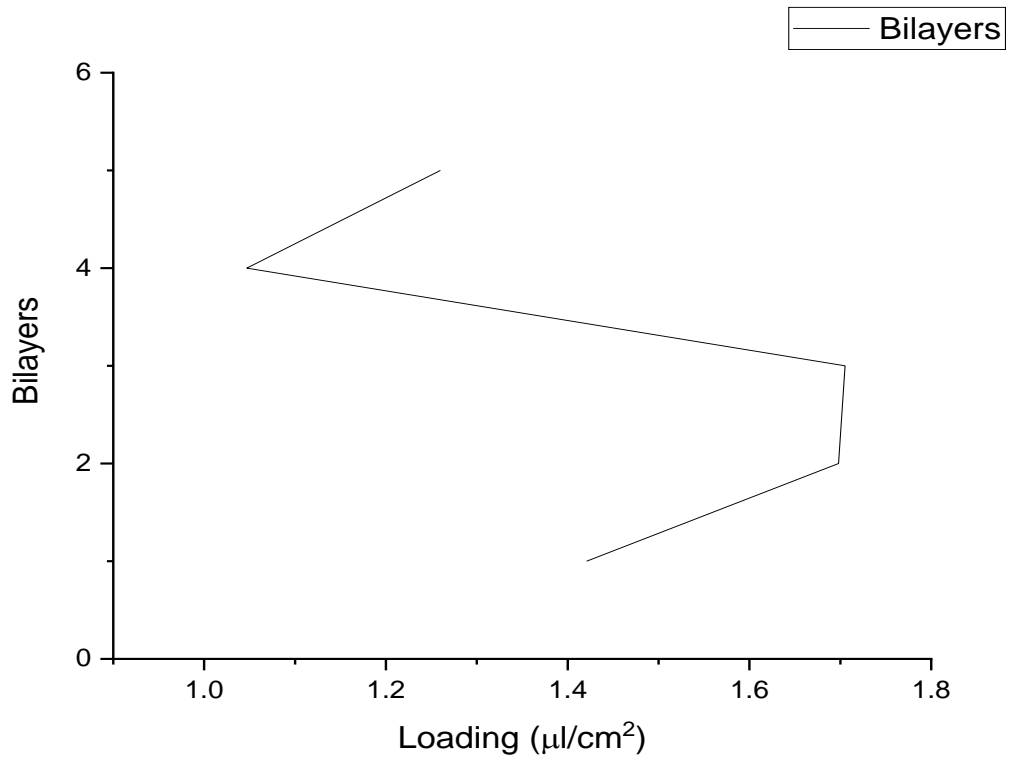
2.2.2 Observations:

(a.) Loading Measurements:

Bilayer	Loading ($\mu\text{l}/\text{cm}^2$)
1	1.42
2	1.69
3	1.70
4	1.04
5	1.26

(2.2)

Table 2.2 The above table shows the cartridge loadings of different Bilayers of PEL Coatings.



(2.16)

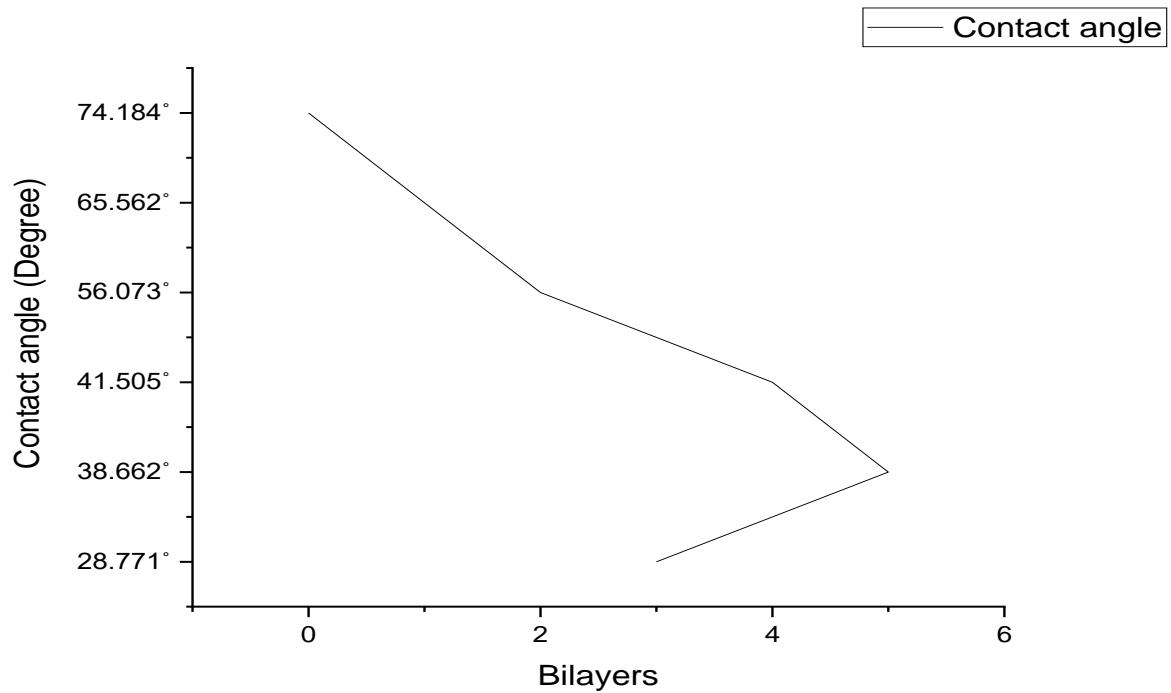
Fig 2.16 shows the variation of loading with the bilayer coating

(a.) Contact Angle Measurements:

Bilayer	Contact angle
Untreated PEL	75.18°
1	65.56°
2	56.07°
3	28.77°
4	41.50°
5	38.66°

(2.3)

Table 2.3 The above table shows the contact angle measurements of different Bilayers of PEL Coatings.



(2.17)

Fig 2.17 shows the variation of contact angle with the bilayer coating.

Inference:

From, the above characterizations it can be seen that there are certain anomalies in reading. The Cartridge loading didn't show the expected trend also the contact angle measurements weren't uniform. So, it was hypothesized that the loss of uniformity in coating is due the methodology followed and it was changed to get a better conductive structure on the plastic substrate. Though the methodology 1 works well for PEL coating for small amount of samples, it fails to deliver the similar effect for bulk coating of many samples in a single stretch.

2.2.3 Methodology -2

Pre-Processing (Bilayer Treatment):

In this experiment different bilayer coatings starting from 1 to 5 bilayers with varied loadings of 1mg, 2mg & 3mg of Ag each consisting of 2 samples is prepared, same as before but the methodology followed for coating is changed.



(2.18)



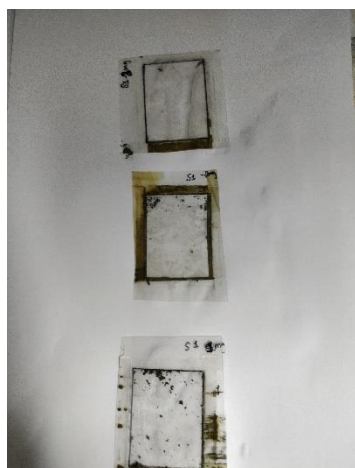
(2.19)

Fig 2.18, 2.19 PEL treatment process, with plasma cleaning, bilayer treatment process for large amount of samples respectively.

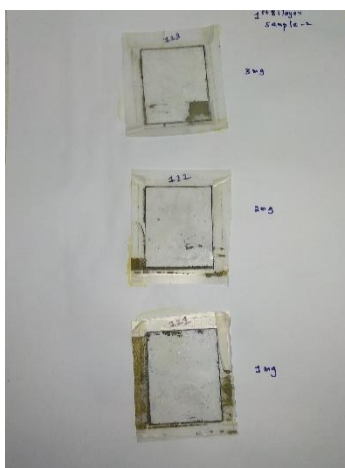
After the plasma cleaning process the samples were PEL treated to obtain different bilayers by the method shown above in Fig 2.19, where the trays were filled with PDDA and the petri dishes with PSS and the samples were dipped in these solutions 5 minutes each sides for even treatment. All 35 samples of OHP sheet (7 samples per batch equating to 5 batches i.e. 5 bilayers) can be treated in a single go unlike methodology 1. The rest of the steps were continued as before.

The Print-Expose-Develop Process is continued on. And the findings are reported below.

After Print-Expose-Develop Process:



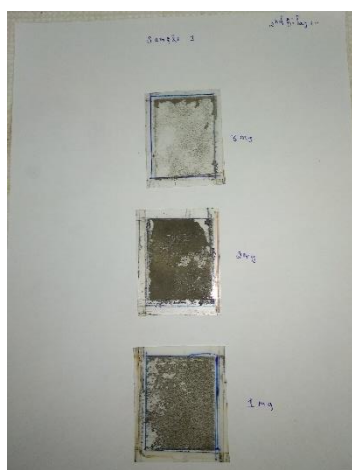
(2.20)



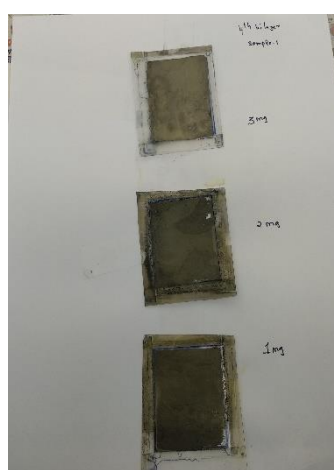
(2.21)



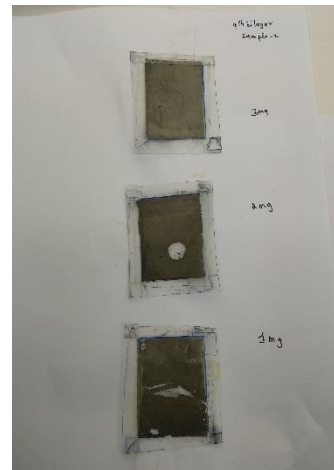
(2.22)



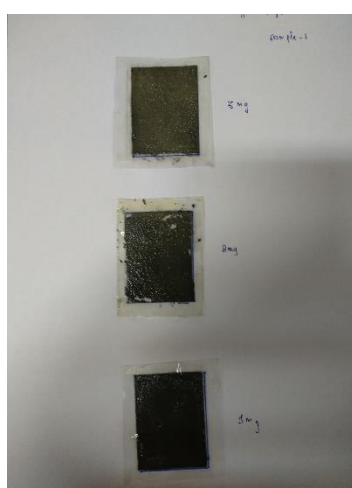
(2.23)



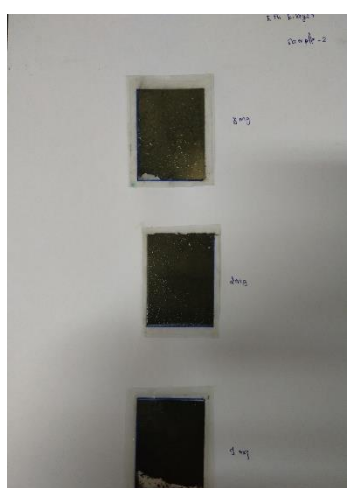
(2.24)



(2.25)



(2.26)



(2.27)

Fig 2.20, 2.21 1st Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.22 2nd Bilayer with 1mg, 2mg & 3mg.

Fig 2.23 3rd Bilayer with 1mg, 2mg & 3mg.

Fig 2.24, 2.25 4th Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.26, 2.27 5th Bilayer with 1mg, 2mg & 3mg with 2 samples each.

From, the above figures it can be seen that there is a formation of uniform conductive structure for 5th, 4th & 3rd Bilayer. And it could also be noted from figures 2.22 & 2.23 that if there is a higher loading for less PEL coated (less adhesive) surface it becomes prone to leaching. The samples were characterized to obtain further insights.

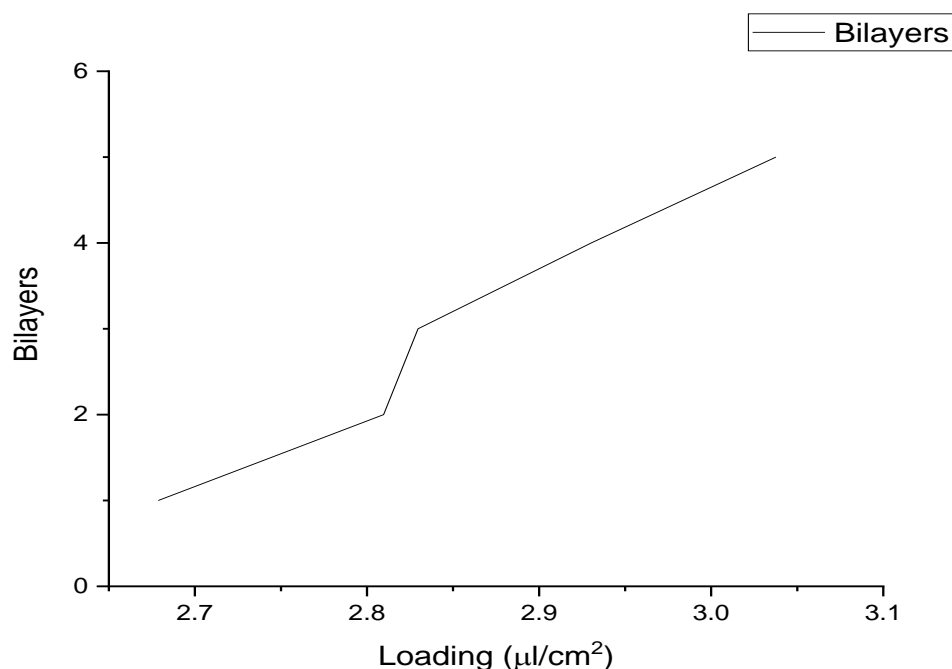
2.2.4 Observations:

(a.) Loading Measurements:

Bilayer	Loading ($\mu\text{l}/\text{cm}^2$)
1	2.67
2	2.80
3	2.82
4	2.93
5	3.03

(2.4)

Table 2.4 The above table shows the cartridge loadings of different Bilayers of PEL Coatings.



(2.28)

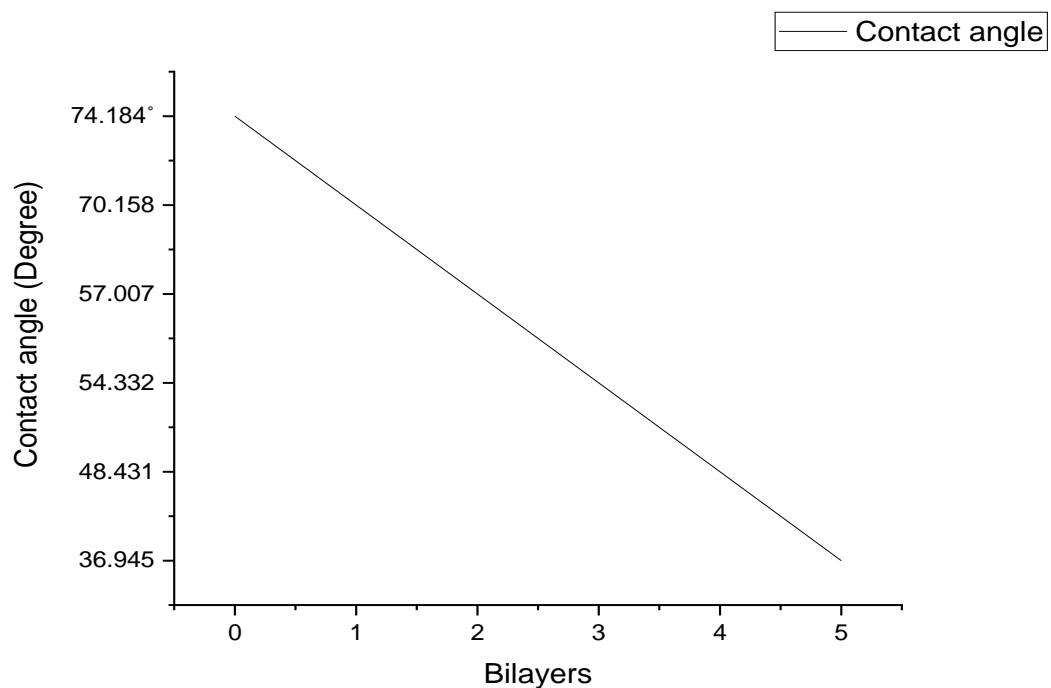
Fig 2.28 shows the variation of loading with the bilayer coating

(a.) Contact Angle Measurements:

Bilayer	Contact angle
Untreated PEL	75.18°
1	70.15°
2	57.00°
3	54.33°
4	48.43°
5	36.94°

(2.5)

Table 2.5 The above table shows the contact angle measurements of different Bilayers of PEL Coatings.



(2.29)

Fig 2.29 shows the variation of contact angle with the bilayer coating.

(c.) Electrical Resistance Measurements:

	Resistance(ohms)					
	Sample-1			Sample-2		
Bilayers	1mg	2mg	3mg	1mg	2mg	3mg
5	6.7	3.3	1.3	6.4	3.7	1.5
4	8.5	3.7	1.7	8.5	3.79	1.24

(2.6)

Table 2.6 The above table shows the resistance values of the conductive structure coated on 5th and 4th Bilayer.

NOTE: All these measurements were taken by four probe point method. Since, there was no clear conductive path below 3rd bilayer of area 2.5*0.4 cm. Its conductivity was checked with 2 probe method and found to be conductive.

Inference:

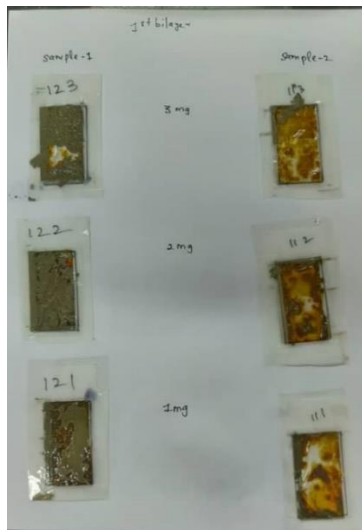
From, the above characterizations it can be seen that the contact angle measurements and loading calculations shows an expected trend. So our hypothesis of irregular coating with methodology 1 is confirmed. Also one important finding **for more Ag Loading more Bilayer of PEL coating should be followed** over here the 3mg loading of Ag seems to be stabilized in 5th Bilayer. The resistance value also seems to be decreasing with increased loading.

Findings:

- A maximum loading of 3mg leaches immediately if the adhesion was not good enough. So, to increase the loading, the bilayer coating has to be increased.
- From the resistance measurements it can be seen that the resistance decreases as the loading increases, and cartridge loading increases as the bilayer coating increases.
- So methodology-2 was adopted for PEL coating on Nafion membrane.

2.3 Inkjet printing of Ag nanowire network on Nafion substrate with different bilayers of PEL coating:

Now, the methodology-2 was adopted for PEL Coating of Nafion samples and the rest of Print-Expose-Develop process as mentioned before was continued on Nafion samples too.



(2.30)



(2.31)



(2.32)



(2.33)



(2.34)

Fig 2.30 1st Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.31 2nd Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.32 3rd Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.33 4th Bilayer with 1mg, 2mg & 3mg with 2 samples each.

Fig 2.34 5th Bilayer with 1mg, 2mg & 3mg with 2 samples each.

From the above figures again it can be confirmed that higher loading leaches in less bilayer coated sample. And over here we can get a uniform conductive structure for 5th, 4th & 3rd Bilayers.

2.3.1 Observations:

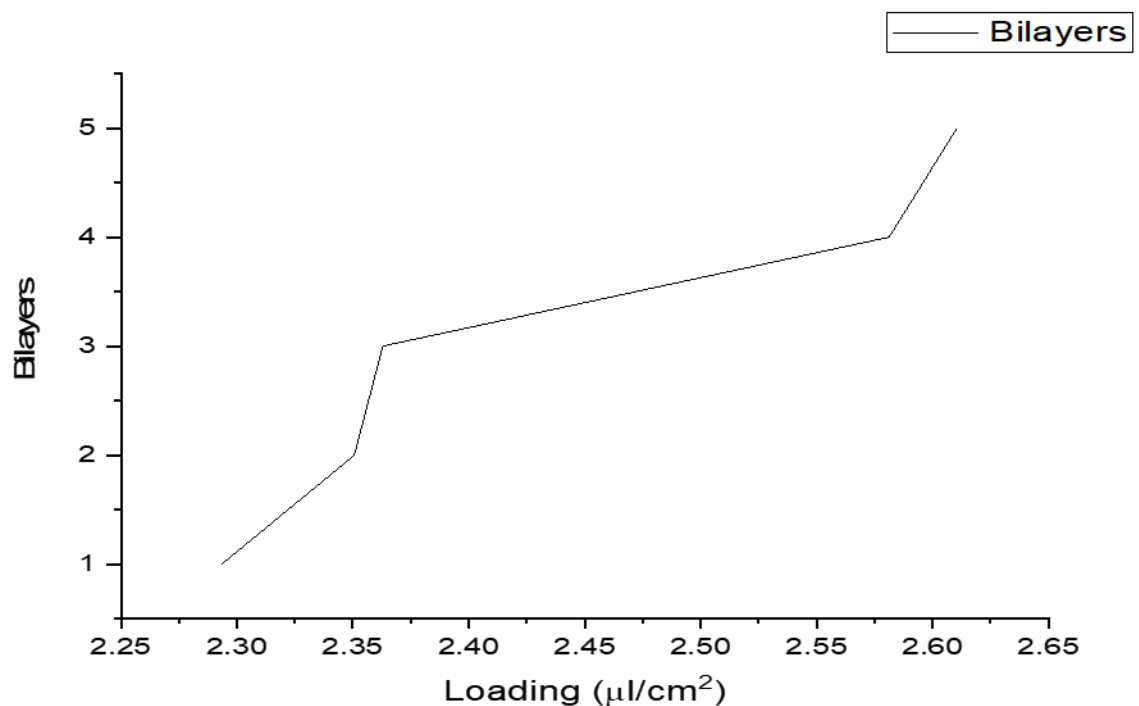
The Printed Nafion samples were characterized to find out resistance and loading.

(a.) Loading Measurements:

Bilayer	Loading ($\mu\text{l}/\text{cm}^2$)
1	2.29
2	2.35
3	2.36
4	2.58
5	2.61

(2.7)

Table 2.7 The above table shows the cartridge loadings of different Bilayers of PEL Coatings.



(2.35)

Fig 2.35 shows the variation of loading with the bilayer coating

It can be seen that it seems to follow the expected trend of increasing loading with increased Bilayers.

(b.) Electrical Resistance Measurement:

	Resistance(ohms)					
	Sample-1			Sample-2		
Bilayers	1mg	2mg	3mg	1mg	2mg	3mg
5	53.6	16.3	1.3	10.4	9.6	4.1
4	3.5	1.3	1.4	8.5	-*	1.3
3	27.4	1.1	-*	2.58	1.42	1.3

(2.8)

Table 2.8 The above table shows the resistance values of the conductive structure coated on 5th, 4th & 3rd Bilayer.

NOTE: All these measurements were taken by four probe point method. Since, there was no clear conductive path below 2nd bilayer of area 2.5*0.4 cm. Its conductivity was checked with 2 probe method and found to be conductive.

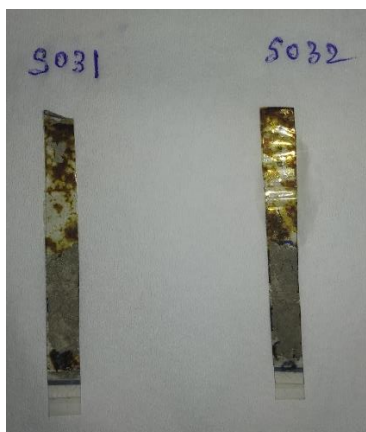
Inference:

From the above findings it can be seen that a uniform conductive structure is formed on Nafion substrate and its conductive nature increases with increased Ag Loading.

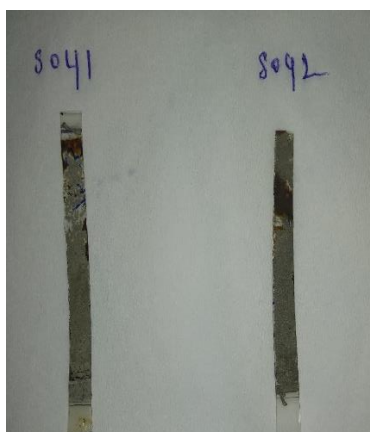
(c.) Acid Stability Test:

For, PEMFC applications it is important that coated Ag nanowire network is stable in acidic medium. To test the stability of the coated Ag network in Nafion substrate it is subjected to acid stability test. In this 2 sample pieces from 5th, 4th & 3rd Bilayer consisting of 3mg Ag loading is taken and dipped in 15ml of 1N HClO₄(Perchloric acid) with a pH of less than 2. It is kept in acidic medium for 1 hour and resistance value of the stable sample was measured before and after dipping in the acidic medium.

*Didn't have a clear conductive path for resistance measurement.



(2.36)



(2.37)



(2.38)

Fig 2.36, 2.37 & 2.38 shows the 3rd, 4th & 5th Bilayer samples after dipping into HClO_4 respectively.

From the above figure it can be seen that the one with 5 Bilayers and 3mg Ag loading is stable in acidic medium and it doesn't leaches off like 3rd and 4th Bilayer. The resistance value was measured.

Resistance Measurement:

Samples	Resistance(ohms)	
	Before dipping in HClO_4	After dipping in HClO_4
S051	3.1	4.4
S052	3	4.3

(2.9)

Table 2.9 The above table shows the resistance values of the conductive structure coated on 5th Bilayer samples S051 & S052 respectively.

Inference:

From, the above resistance value it can be seen that the resistance value didn't change much before and after dipping into the acidic medium. The Ag-Nanowire structure appears to be stable in acidic solution for 5 bilayer PEL coating for 3mg Ag loading.

Therefore the one with 5 Bilayer's and 3mg Ag loading was chosen as the ideal sample for platinum deposition.

2.4 Electrochemical experiments:

2.4.1 Platinum electrodeposition on silver nanowire

Setup for electrodeposition

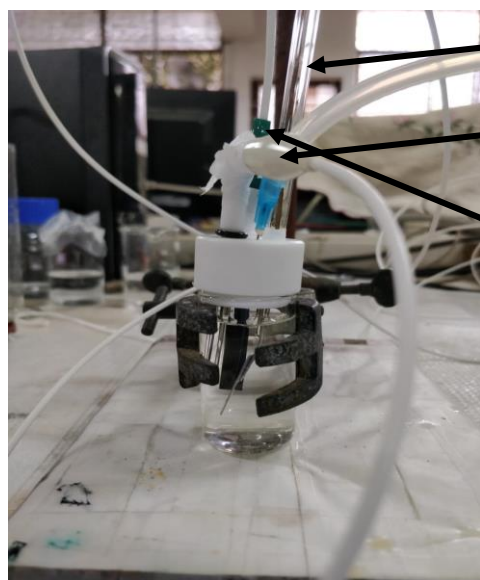
K₂PtCl₄ and NaCl were used as precursor for platinum and supporting electrolyte respectively. 20 ml solution of 3mM K₂PtCl₄ and 0.5M NaCl were taken in an electrochemical cell. pH of the solution was checked using pH meter (LABMAN Scientific instruments) and adjusted to 4 with the help of HClO₄ and NaOH. Figure 2.39 below shows the electrochemical setup used. CHI 608D Electrochemical analyzer from CH Instruments was used to control the electrodeposition of platinum. The parameters and reactions for platinum deposition are described as below:

Working electrode (Cathode): substrate on which platinum is to be deposited

Counter electrode (Anode): Platinum wire

Reference electrode: Ag/AgCl/KCl (1M)

Electrolyte: K₂PtCl₄ + 0.5M NaCl



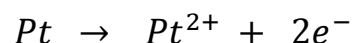
(2.39)

Counter Electrode

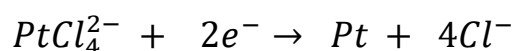
Reference Electrode

Working Electrode

Anode (counter electrode):



Cathode (working electrode):



Platinum gets reduced on the Ag Nanowire surface.

2.4.2 Platinum electrodeposition using chronoamperometry

To calculate the exact amount of platinum deposition through electrochemistry, it was decided to keep track of current v/s time by chronoamperometry, so that corresponding change can give the exact amount of platinum reduced with the help of Faraday's law. Moreover, the loading of platinum used to calculate ECSA in platinum step electrodeposition was as per the assumed model. In that context, chronoamperometry provides the correct value of platinum electrodeposited.



(2.40)

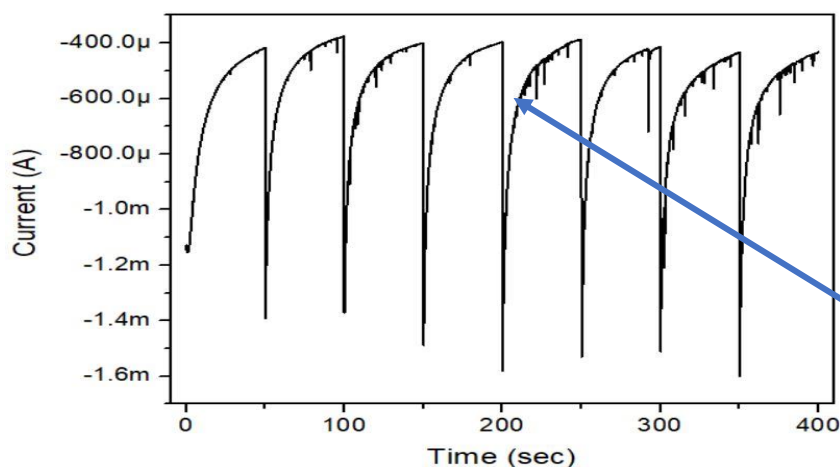
Fig 2.40 shows Platinum-deposited Ag Nanowire conductive layer.

Chronoamperometry Parameters	
Initial E (V)	-0.799
High E(V)	-0.78
Initial Step Polarity	Negative
Number of steps	1
Pulse Width(sec)	50
Sample Interval(sec)	0.02
Quiet Time(sec)	2
Sensitivity(A/V)	1*e-003

(2.10)

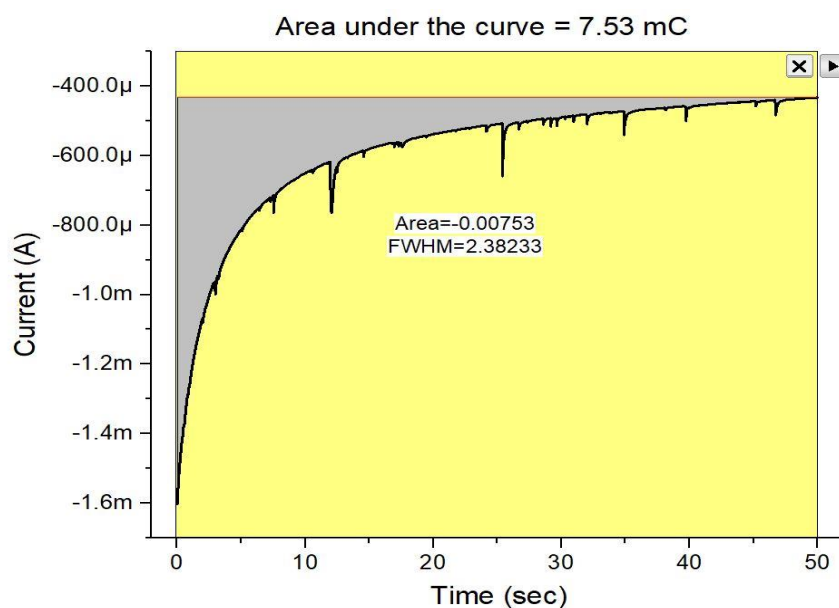
Table 2.10 Shows the CA Parameters for Platinum deposition.

From the above figure 2.40 it can be seen that some region of the sample turned black. This is the one where Pt has been deposited.



(2.41)

Pt deposition



(2.42)

Fig 2.41 shows the Chronoamperometry curve for Pt deposition graph

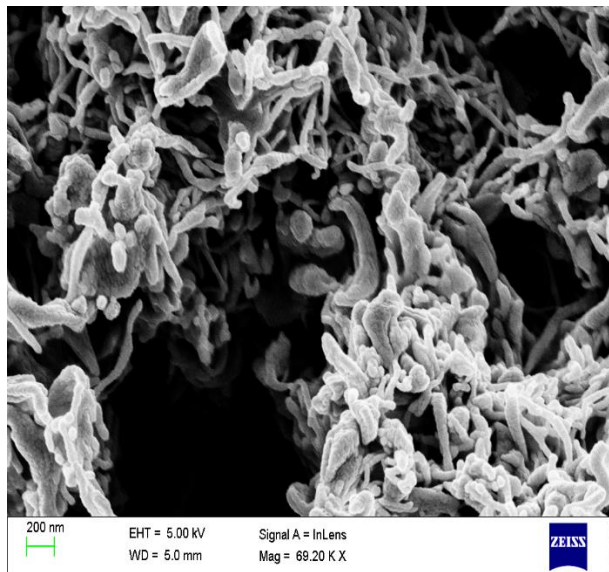
Fig 2.42 shows the area under I vs t curve.

The above shown Fig 2.41 shows 8 cycles of Pt coating. This is a one way coating process where Pt is deposited and in the place of H_2 desorption step after one cycle of Pt deposition the sample is washed with water and blown with N_2 . The process is of 50 sec/cycle. The amount of Pt coated is calculated from faraday's second law, and it turns out to be $\sim 7.8 \mu g/cm^2$ i.e. $> 10 \mu g/cm^2$ per cycle. Now the sample after CA is subjected to SEM characterization.

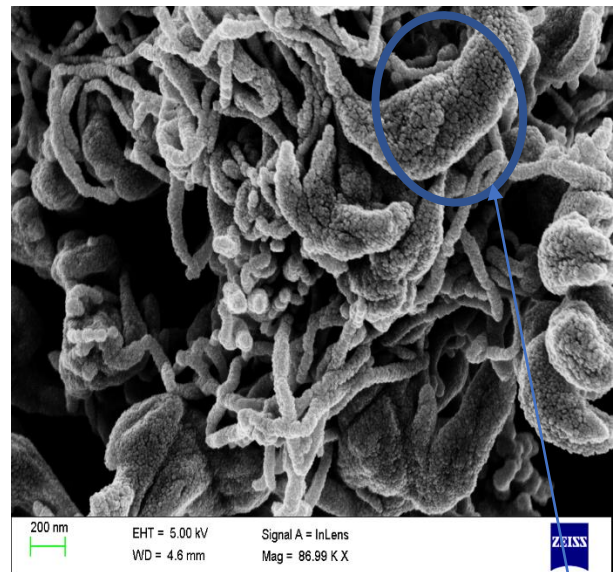
The sample turned black after platinum deposition but maintained similar conductivity as that of before, indicating that platinum does not influence the percolating silver nanowire network. The trend of decreasing charge value for platinum deposition in chronoamperometry can be attributed to the unwanted ions and impurities, which might have caused hindrance in electrochemical reactions.

The first cycle is quantitatively different to the next seven cycles, because, in the first cycle, platinum deposition happens on silver, while in the rest of them, platinum deposits on the already deposited platinum.

Surface Characterization:



(2.43)



(2.44)

Figure 2.43 & 2.44 shows the FESEM images before and after Chonoamperometry respectively.

Granular Pt formation over the Ag percolating structure

From the above figures it can be seen that figure 2.43 has a porous Ag Nanowire network and in figure 2.44 which is after Pt-deposition on Ag Nanowire structure. Over here granular deposition of Pt can be seen. And the thickness of this granular coated Pt percolating Ag nanowire's thickness is greater than 200nm.

Nanowires beneath were intact, Pt deposition was uniform on the nanowire substrate.

Resistance studies:

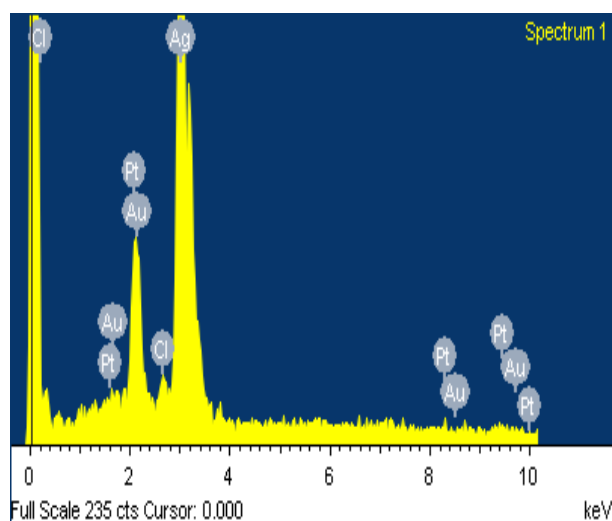
	Resistance(ohms)	
	Sample-1	Sample-2
Before CA	3.48	3.49
After CA	13.41	13.55

(2.11)

Table 2.11 The above table shows the variation of resistance of 3mg Ag loaded sample before and after chronoamperometry.

From the above table it can be seen that there is quite increase in the resistance value after CA. This can be attributed to the step of washing with water and blowing with N₂. Since, it can break the conductive path of the Ag Nanowire.

Elemental analysis of Pt:



(2.45)

Element	Weight%	Atomic%
Cl K	0.26	0.87
Ag L	81.27	88.09
Pt M	13.00	7.79
Au M	5.46	3.24

(2.12)

Fig 2.45 Elemental analysis of platinum deposited silver nanowire on Nafion membrane.

Table 2.12 shows the atomic and weight percent of compounds present in the substrate

Inference:

In the studies carried out before it was found that EDS couldn't detect platinum, for 1mg loading of Ag. EDS penetrates till 1 μm and can usually detect till 1% limit. So, samples were characterized by XPS and XRD to check platinum presence. But in this study with 3mg Ag loading the Pt was detected in EDS analysis itself and was found out to be Pt/Ag = 0.08741%.

Thus 3mg Ag loading was preferable for Pt deposition.

2.4.3 Cyclic Voltammetry of Pt deposited Ag Nanowire substrate:

The presence of electrochemically active platinum was confirmed with the help of cyclic voltammetry. Cyclic voltammetry is commonly used as a tool in fuel cell research and provides insight about the area which is accessible electrochemically. Preliminary experiments were conducted to get optimum parameters for characterizing platinum by cyclic voltammetry (CV) in 0.1M HClO₄. This area is used to calculate electrochemically active surface area (ECSA), which is defined as:

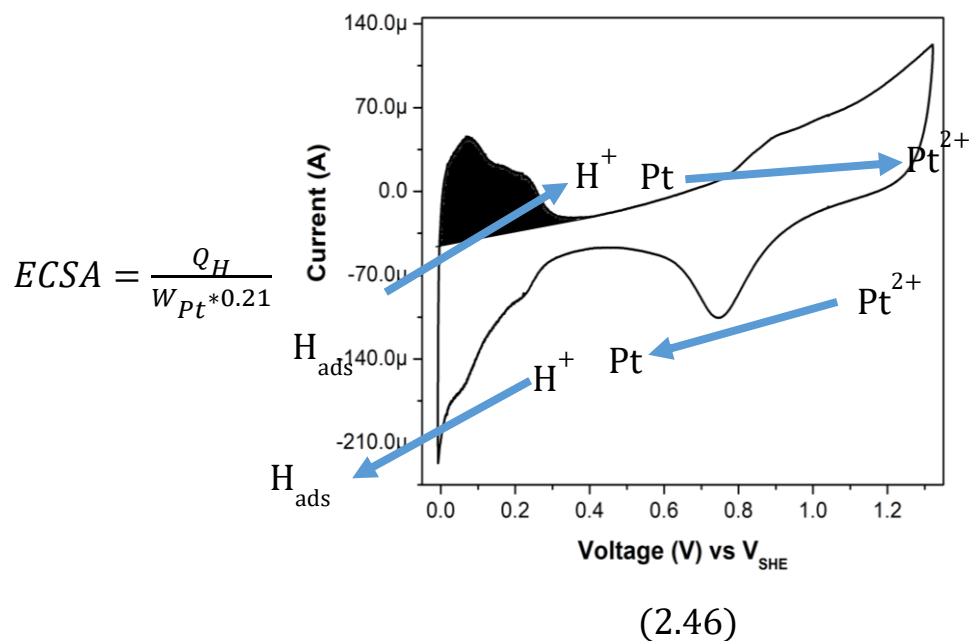
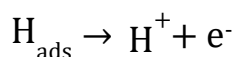


Fig 2.46 shows the Cyclic Voltammetry for pure elements.

Where W_{Pt} (mg Pt/cm² geometric area) is the platinum loading at the working electrode. Q_H stands for charge consumed for the electro-oxidation of adsorbed hydrogen atoms on platinum surface, which is calculated from the area of the hydrogen desorption peak in the CV curve (mC/cm²).

During the reduction of platinum, protons from the acid are adsorbed at the surface of the electrode. During the oxidation, these atoms of hydrogen are desorbed according to the following electrochemical reaction:



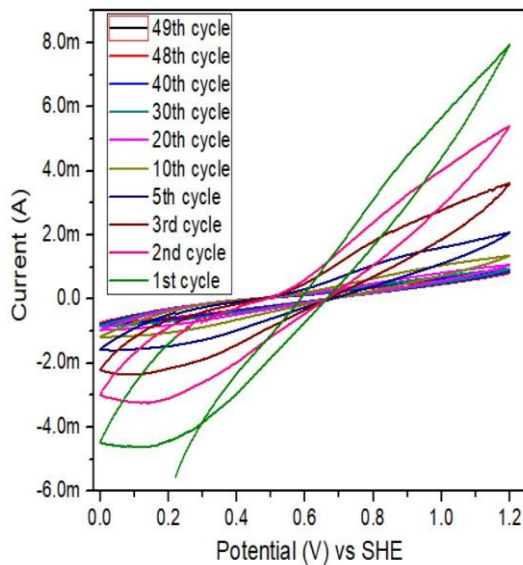
The measure of the number of electrons liberated during the oxidation of platinum for low potentials gives the number of hydrogen atoms desorbed and thus the number of adsorption sites present on the electrode's surface. This defines the active surface of the electrode. The presence of active platinum sites gives rise to a peaks.

Cyclic Voltammetry Parameters	
Initial E (V)	0
High E(V)	0.98
Low E(V)	-0.22
Final E(V)	0
Initial scan Polarity	Positive
Scan Rate(V/s)	0.05
Sweep Segments	100
Sample Interval(V)	0.01
Quiet Time(sec)	2
Sensitivity(A/V)	1*e-003

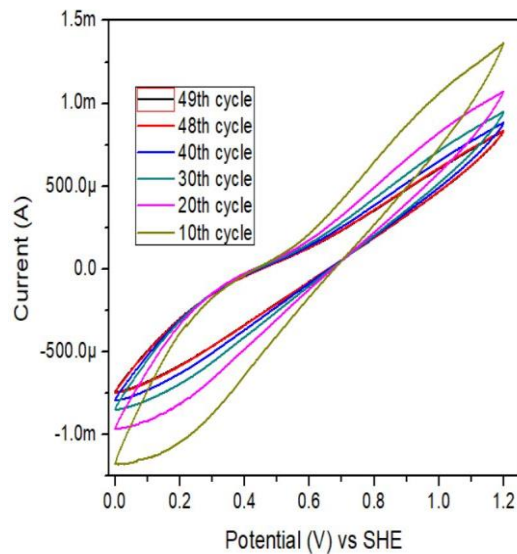
(2.13)

Table 2.13 Shows the Cyclic Voltammetry parameters

CV curves analysis:



(2.47)

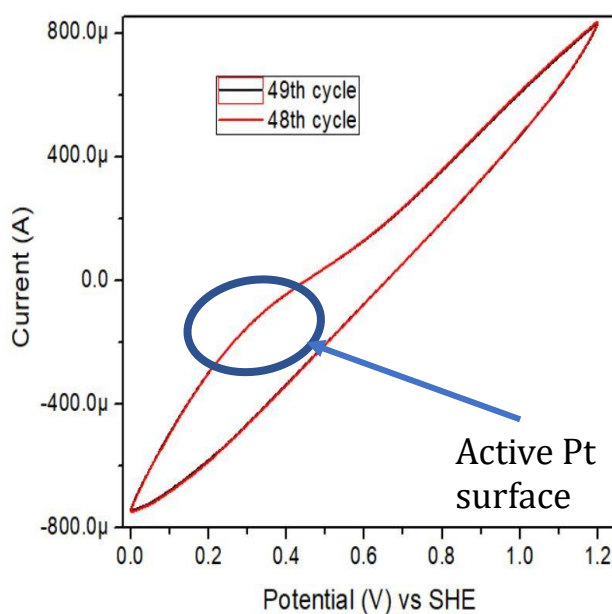


(2.48)

Fig 2.47 and 2.48 shows the Cyclic Voltammetry of Pt deposited AgNW substrate.

From figure 2.47 it can be seen that the current value continuously fluctuates starting with a maximum and minimum of 8mA and -6.3 mA with the initial cycle. This continuous fluctuation indicates the leaching of Pt from the coated surface. And continuous reduction in the current value in the first 10 cycles also shows the continuous leaching of platinum. Fig 2.48 also shows the reduction maximum and minimum value but starting from

the 10th cycle to 49th cycle. Over here too the reduction signifies leaching of Pt from the surface but there is no aggressive leaching like in the first 10 cycles. The leaching is trying to stabilize after the first 10 cycles.

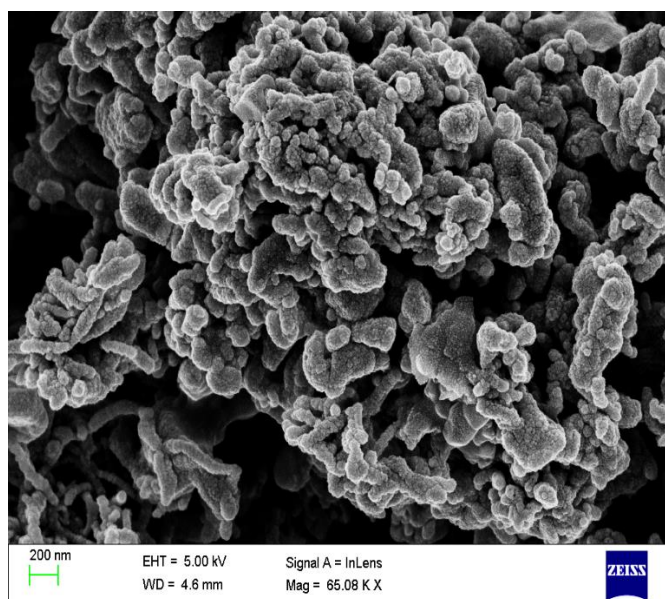


(2.49)

Fig 2.49 shows Cyclic Voltammetry curve from the 48th-49th cycle

In Fig 2.49, it can be seen that there is a stable CV curve, this indicates that whatever Pt was leaching has stopped till 47th cycle and whatever has been left in 48th cycle is the active Pt surface area.

Surface Characterization:



(2.50)

Figure 2.50 shows the FESEM image after Cyclic Voltammetry. From, the above FESEM image it can be seen that the intact nanowire structure that was present before is absent now. And the conductive structure is absent after cyclic voltammetry. It appears to be that all the NW clustered up i.e. the presence of platinum is in the form of lumpy structure.

Resistance studies:

	Resistance(ohms)	
	Sample-1	Sample-2
Before CA	3.48	3.49
After CA	13.41	13.55
After CV	552.6	484.74

(2.14)

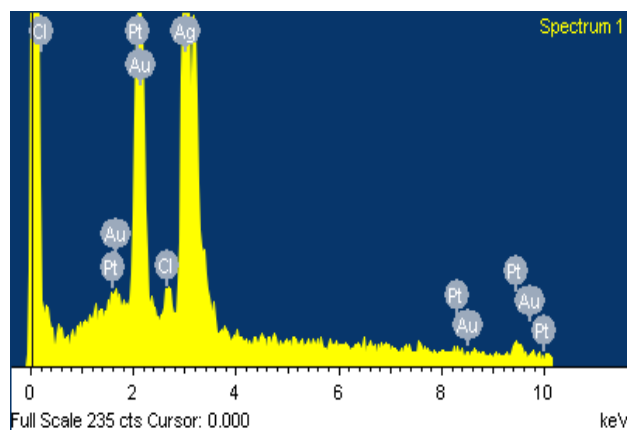
Table 2.14 The above table shows the variation of resistance of 3mg Ag loaded sample before and after chronoamperometry and after cyclic voltammetry.

From the above table, it can be seen that resistance value shoots up after cyclic voltammetry. And from this it is evident that it is losing its conductive structure. This can be attributed to either to the acidity of the acidic solution in cyclic voltammetry or due to the passage of voltage through the strip. But from the acid stability test we concluded that the structure is intact and conductive after dipping in HClO_4 solution for 1 hour.

This can also be attributed to leaching of Ag from the substrate. So it was concluded that the problem must be with the passage of voltage.

To confirm whether the particles on the top of nanowire are platinum or not, elemental analysis of this sample was done.

Elemental analysis of Pt:



(2.51)

Element	Weight%	Atomic%
Cl K	0.50	1.76
Ag L	68.25	78.42
Pt M	25.60	16.26
Au M	5.65	3.55

(2.15)

Fig 2.51 Elemental analysis of platinum deposited silver nanowire on Nafion membrane after CV.

Table 2.15 shows the atomic and weight percent of compounds present in the substrate

Inference:

Through EDS presence of Pt can be seen, but it can also be noted that the atomic percent of Pt has reduced compared with the EDS before CV.

Moreover, the elemental analysis reveals the presence of chlorine. Since it was concluded from the acid stability test that 3mg loaded Ag is stable in acidic environment it was suspected the passage of voltage is making it to lose its conductive structure. And it can also be seen from the FESEM image the nanowire restructures itself into a lumpy structure.

Chapter-3

Conclusions

In the attempt of making conductive, porous and low-cost catalyst for PEMFC, as a first step, *In-situ* synthesis of conductive silver nanowire network was adapted on Nafion membrane after surface modification using plasma cleaning and layer by layer poly-electrolyte (PEL) application to yield conductivity $< 5 \text{ ohm/sq}$. And with multiple coating of PEL bilayers and multiple loading values starting from 1 mg/cm^2 to 3 mg/cm^2 , all were tried to find an optimized Bilayer coating and loading values and it was concluded that 5 bilayers of PEL coating with 3 mg/cm^2 of Ag loading formed a stable film on Nafion membrane and it was tested in acidic conditions. Further, to use this as a conductive backbone for electrodepositing platinum on it, the self-terminating platinum electrodeposition process was used. One of the important finding of this study was 3 mg/cm^2 of Ag loading was identifiable in EDS analysis compared to previous study where 1 mg/cm^2 failed to show the Pt presence. Chronoamperometry technique was used to coat platinum on Ag surface. After, the conductive silver nanowire structures were used as substrates for platinum deposition using Chronoamperometry approach, Cyclic Voltammetry was carried out to find the active Pt surface and it was found out that the Pt leaches away and the substrate shows a low ECSA and the silver nanowire structure loses its conductivity due to restructuring. And this loss in conductivity is believed to be the passage of voltage through the substrate during Cyclic Voltammetry.

Chapter-4

Future Scope

Even though, the presence of platinum is detected in chronoamperometry, the exact reason for electrocatalytically inactivity of platinum is to be investigated. We can increase the active surface area of Pt by increasing the cycles of Pt deposition from 8 cycles to 16 cycles. And the intact structure of Ag nanowire could be covered with gold or copper before depositing platinum to avoid breaking of the nanowires and subsequent increase in resistance can be avoided. The effect of passage of voltage in an Ag coated substrate should also be investigated. Different loading combinations along with different Pt deposition cycles should be carried out to find out the optimized value. Once the active and stable platinum is obtained, the durability of the catalyst layer must be checked for 1000 cycles since fuel cell vehicles have to undergo several cycles of start-up and shut-down. Next to that, Membrane Electrode Assembly (MEA) should be fabricated and polarization curve of the assembly must be obtained in the fuel test station to check the performance of the printed catalyst layer for comparing it with that of conventional PEMFCs.

Appendix A: Loading Calculations & Developer solution preparation

Cartridge loading Calculation: For Nafion membrane

Bilayer	Loading ($\mu\text{l}/\text{cm}^2$)
1	2.29
2	2.35
3	2.36
4	2.58
5	2.61

(A.1)

Table A.1 shows the linear increase in the loading value with Bilayer Coating

$$\begin{aligned}\text{For 2M and 5ml AgNO}_3 &= 2 \text{ mol lit}^{-1} * (5*10^{-3}) \text{ lit} * 170 \text{ g mol}^{-1} \\ &= 1.698 \text{ g of AgNO}_3\end{aligned}$$

If 169.8g of AgNO₃ contains 109.8g of Ag

$$1.698\text{g of AgNO}_3 \text{ contains } = 1.0798\text{g of Ag}$$

If 5 ml contains 1.0798g of Ag

$$1 \mu\text{l contains } 0.2156\text{mg of Ag}$$

For e.g. for the 1st Bilayer the loading is $2.29 \mu\text{l}/\text{cm}^2$

$$\begin{aligned}\text{Therefore 1 print gives} &= (0.2156*10^{-3}) \text{ g of Ag} * 2.29 \mu\text{l}/\text{cm}^2 \\ &= 0.4944 \text{ mg Ag}\end{aligned}$$

If 0.4944 mg Ag is obtained for 1 print

$$1 \text{ mg Ag loading is obtained from } 2.022 \text{ prints}$$

$$\text{i.e. } \sim 2 \text{ prints} \longrightarrow \text{KAAK}$$

Similarly no of prints required was calculated for all Ag loadings and all bilayers.

Bilayers	Number of prints	Number of prints	Number of prints
	1mg Ag Loading	2mg Ag Loading	3mg Ag Loading
1	2	4	6
2	2	4	6
3	2	4	6
4	2	4	5
5	2	4	5

(A.2)

Table A.2 shows the number of prints to be done on the substrate.

Here, 6 means KKKKAAAAAkk. This pattern is followed because in literature it was found that continuous coating of K provides better conductive bed than the alternative coating. Also it can be noted that with increasing Bilayer the number of prints decreases.

Preparation of Developer solution ID-78:

The composition of ID78 developer has been given below

To prepare 200ml of developer solution.

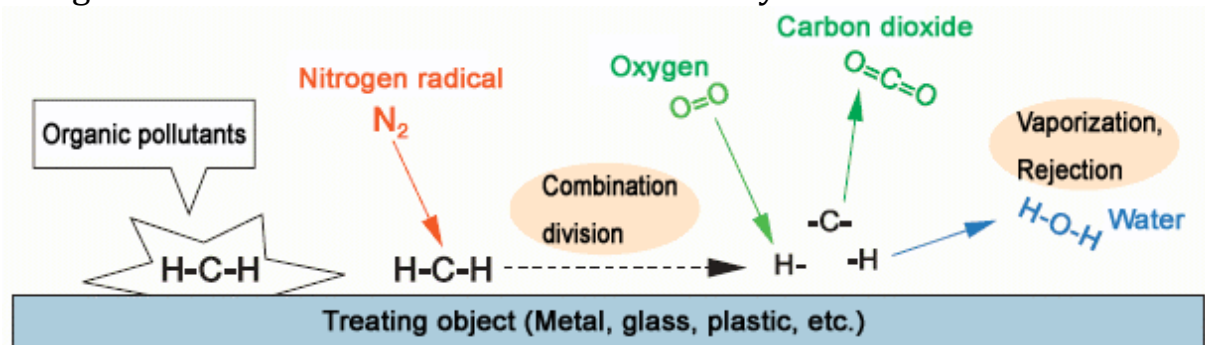
10 g of Sodium Sulphite, 2.4 g of Hydroquinone, 12.4 g of Na₂CO₃ (desicated), 0.1 g of Phenidone & 0.08 g of KBr.

Should be added to 200 ml of DI water and sonicated properly to ensure complete dissolution of solutes in the water.

Over here Phenidone is the required developer to carry out the Ag nucleation process.

Appendix B: Plasma Cleaner

Plasma cleaning is the process of removing all organic matter from the surface of an object through the use of an ionized gas called plasma. This is generally performed in a vacuum chamber utilizing oxygen and/or argon gas. The cleaning process is an environmentally safe process as there are no harsh chemicals involved. Plasma often leaves a free radical on the surface being cleaned to further increase the bondability of that surface.



(B.1)

Figure B.1 shows the plasma cleaning process in detail

Our goal of using plasma cleaner is to decrease the contact angle to a very low value. But since plasma cleaning is a temporary effect this is carried out before PEL treatment and immediately after treatment the plasma treated sample is dropped in PDDA solution to start with the PEL coating.

Oxygen Argon Plasma Cleaning VS. Hydrogen Plasma Clean

Utilizing different gaseous species (oxygen, argon, nitrogen, hydrogen, helium, etc.), plasma can alter a variety of characteristics on the substrate surface. These characteristics include but aren't limited to:

- Modified surface tension/surface energy/contact angle properties
- Improved inter-surface bonding and adhesion
- Hydrogen plasma is extremely effective at removing oxide from glass or metal products
- Altered surface wettability to create hydrophilicity or hydrophobia (increased or decreased adhesion of liquids) – useful in pre-processing, painting and coating applications
- Coating processes: adhesion, wettability, corrosion and wear resistance, electrical conductivity and insulation, magnetic response, reflective/anti-reflective, anti-microbial, anti-scratch, waterproofing, tinting, etc.

Appendix C: Poly Vinyl Alcohol coating of OHP substrate

Instead of the regular PEL coating to make the surface hydrophilic PVA (poly vinyl alcohol) treatment of the OHP sheet samples were explored and its contact angle were measured and compared with the PEL treated one.

Poly (vinyl alcohol) (PVA):

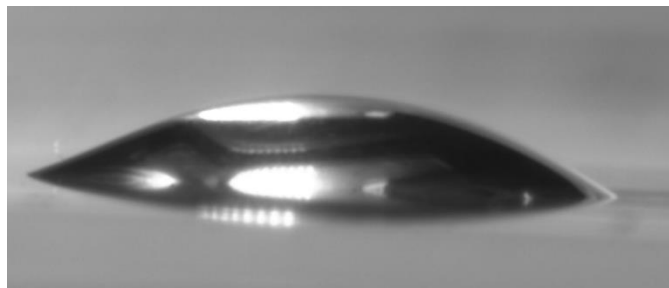
PVA is a water-soluble synthetic polymer. It has the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is used in papermaking, textiles, and a variety of coatings. It is white (colourless) and odourless. It is sometimes supplied as beads or as solutions in water. It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents.

Typically a 5% solution of polyvinyl alcohol exhibits a pH in the range of 5.0 to 6.5. Polyvinyl alcohol has a melting point of 180 to 190°C. It has a molecular weight of between 26,300 and 30,000, and a degree of hydrolysis of 86.5 to 89%. The primary raw material used in the manufacture of polyvinyl alcohol is vinyl acetate monomer. It is manufactured by the polymerization of vinyl acetate followed by partial hydrolysis. The process of hydrolysis is based on the partial replacement of ester group in vinyl acetate with the hydroxyl group, and is completed in the presence of aqueous sodium hydroxide. Following gradual addition of the aqueous saponification agent. Polyvinyl alcohol is precipitated, washed and dried. The degree of hydrolysis is determined by the time point at which the saponification reaction is stopped.

Procedure:

- 1 wt% PVA solution was prepared by dissolving powder of PVA in DI water.
- The beaker containing the PVA solution is magnetically stirred on Tarson's Hotop-Digital Hot Plate at rpms of 1000 and a temperature of 70°C. It was left overnight (stirred for around 17 hours).
- After getting the required homogenous solution the PET sheet surfaces were cleaned with IPA solution and kept inside hot air oven for 40 minutes at 110° C.
- Then it was plasma treated for 5 minutes and immersed in PVA solution for 10-15 minutes. 5. After that, it was dried in ambient conditions. Then, it was heated at 110°C for 15 minutes on Hot Plate.
- Later, it was cooled to room temperature, and contact angle measurements were taken.

Contact angle measurement:



(C.1)

Figure C.1 shows a water drop on the PVA treated substrate captured by contact-angle goniometer,

Using the above picture any drop analysis tool is used to obtain the contact angle. We used Image J to analyse the droplet and the contact angle turned out to be $31.33^\circ \pm 3^\circ$. Which was equivalent to the 5th bilayer of PEL.

Inference:

From the above discussion it can be seen that the contact angle has been reduced to the desired level with less laborious path compared to PEL treatment to obtain 5 bilayer. But, for PEMFC application porosity of the coated structure is a must thing. So, the porous structure can be obtained by providing cross-linking. Some of the crosslinking alternatives is provided by Amit Kumar Sonker, Kalpana Rathore and Vivek Verma et al.

Some of the cross linkers are **Glutaraldehyde, Maleic acid, Fumaric acid, Malic acid, Sulfosuccinic acid, Phthalic acid, Iso-phthalic acid, Terephthalic acid, Aconitic acid (cis- and trans-), Citric acid, Hexamethylene diisocyanate, Boric acid.**

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