FABRICATION OF FLEXIBLE ELECTRODE FOR PEMFC USING INKJET PRINTING

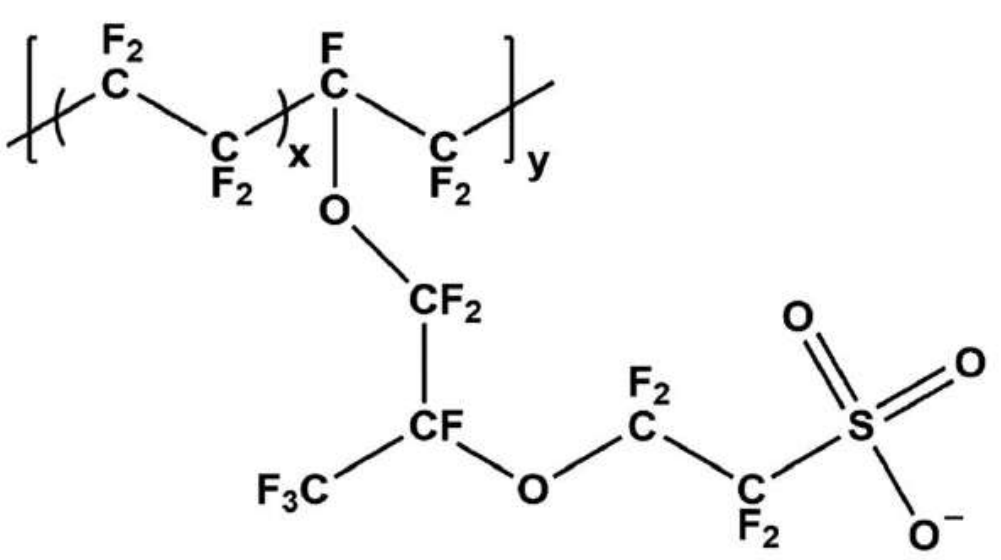
Under the guidance of
Dr. S. Venugopal
Associate Professor
Department of Chemical Engineering
Indian Institute of Science
BANGALORE-560012

Submitted by
Varshan Kumar S
B.Tech, Chemical Engineering
SASTRA Deemed-to-be University

Print-Expose-Develop Process:

Representation of Print-Expose-Develop technique based on aqueous salt printing

Nafion membrane:

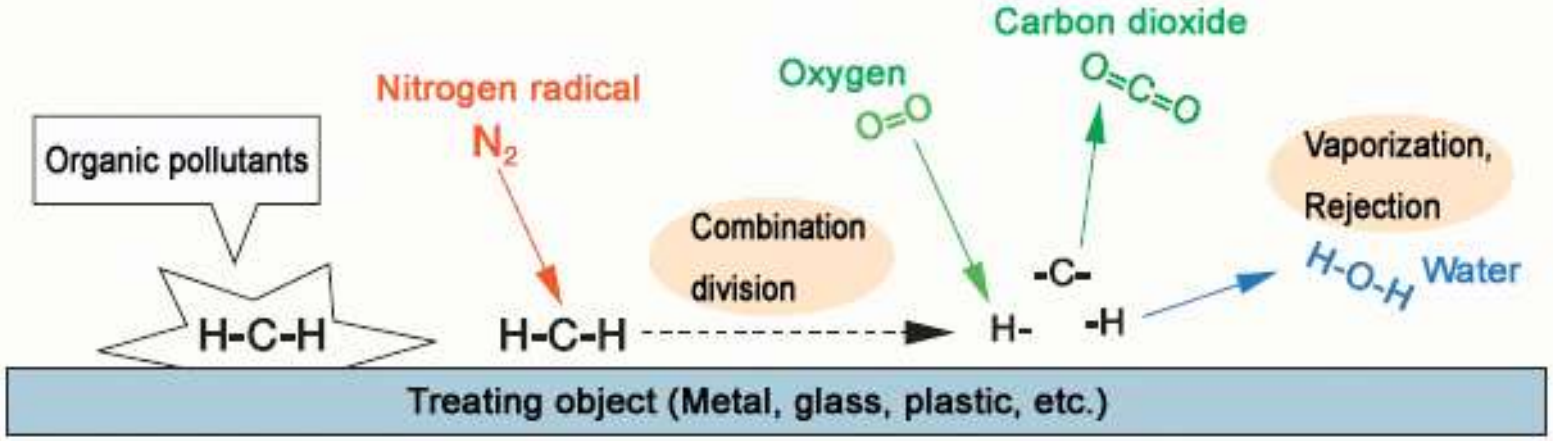


Nafion membrane chemical structure

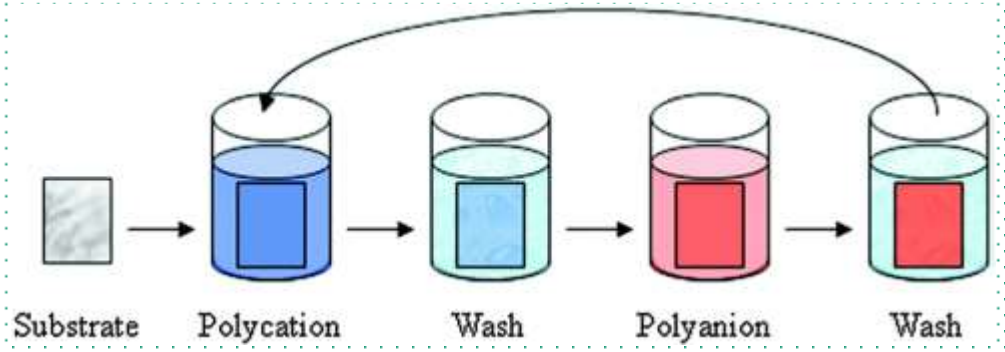
- Contact angle 111.8°
- Preliminary experiments to improve wettability

Pre-treatment to improve wettability:

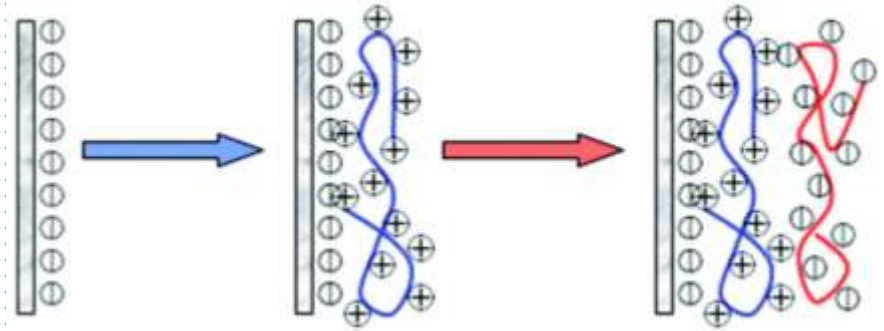
Plasma treatment (Surface cleaning)



Layer by layer PEL



PDDA PSS



Inkjet Printing of Silver nanowire network on plastic substrate:

- Concentrations: 2M of $AgNO_3$ & 4M of KX(95%-KBr,5%-KI)
- OHP sheet- 100µ thickness
- Layer-by-Layer Assembly(LBL) of PEL coating(PDDA & PSS) which is continued on alternatively to finish 5 bilayers.
- With a loading of 3mg/cm^2-KKKKAAAAAAK, the print-expose-develop process is continued on.

Fig 1. Spreading of drop across the substrate was compared by dropcasting 5µL drop of water onto an untreated PEL sheet and PEL coated OHP sheet.

Fig 2. shows the Print, Expose and Develop process of inkjet printing of nanostructure.

Surface characterization:

- To characterize the prepared conductive, porous nanowire structure it is subjected to SEM imaging.

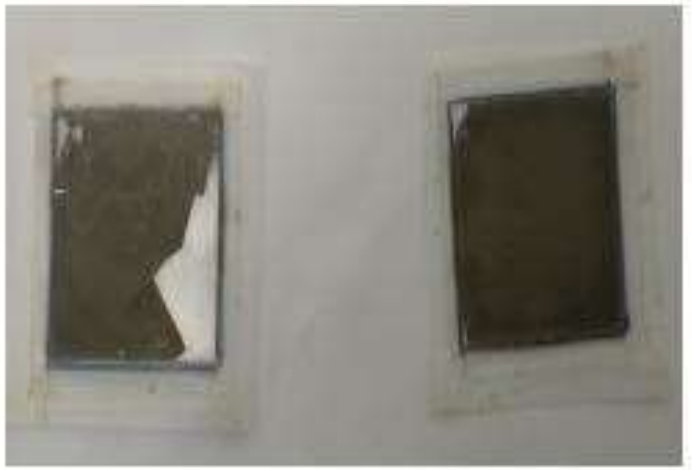


Fig 3. The dried conductive nanowire substrate is shown

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

Table.1 Resistance values of the samples

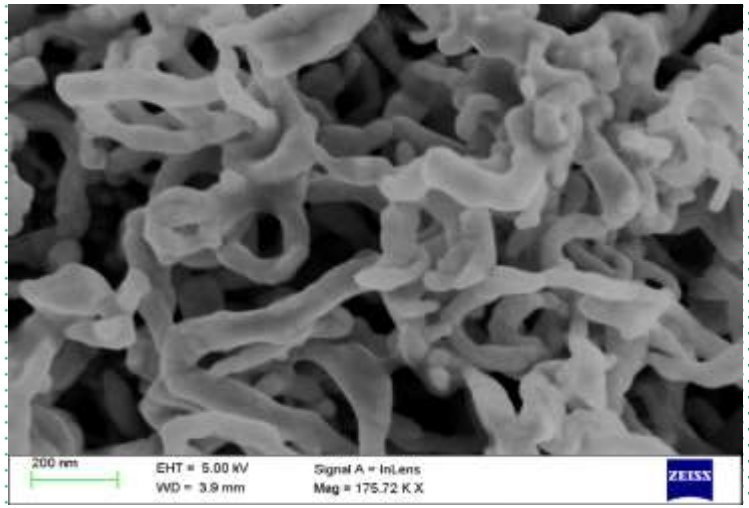


Fig 4. The FESEM image of the developed substrate shows a uniform covering of silver nanowire network on PEL coated PE sheet.

Inference:

Since, the sample (1) on the left side of Fig 3 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.

With varied bilayer coating:

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

- **Methodology 1:**

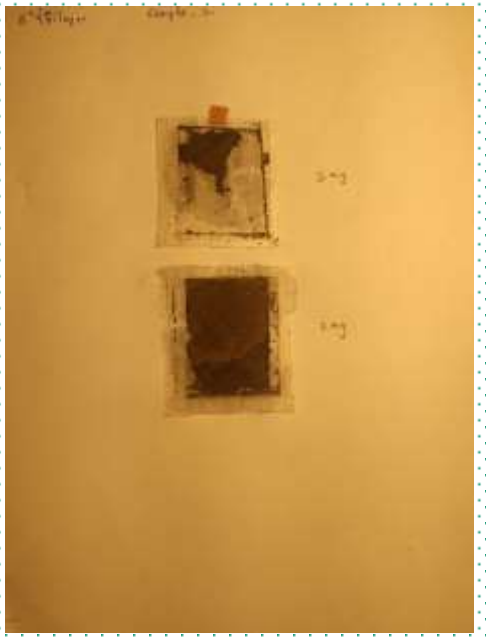
With varied bilayer coating:

Observations:

- 1st Bilayer:

2nd Bilayer:

3rd Bilayer:



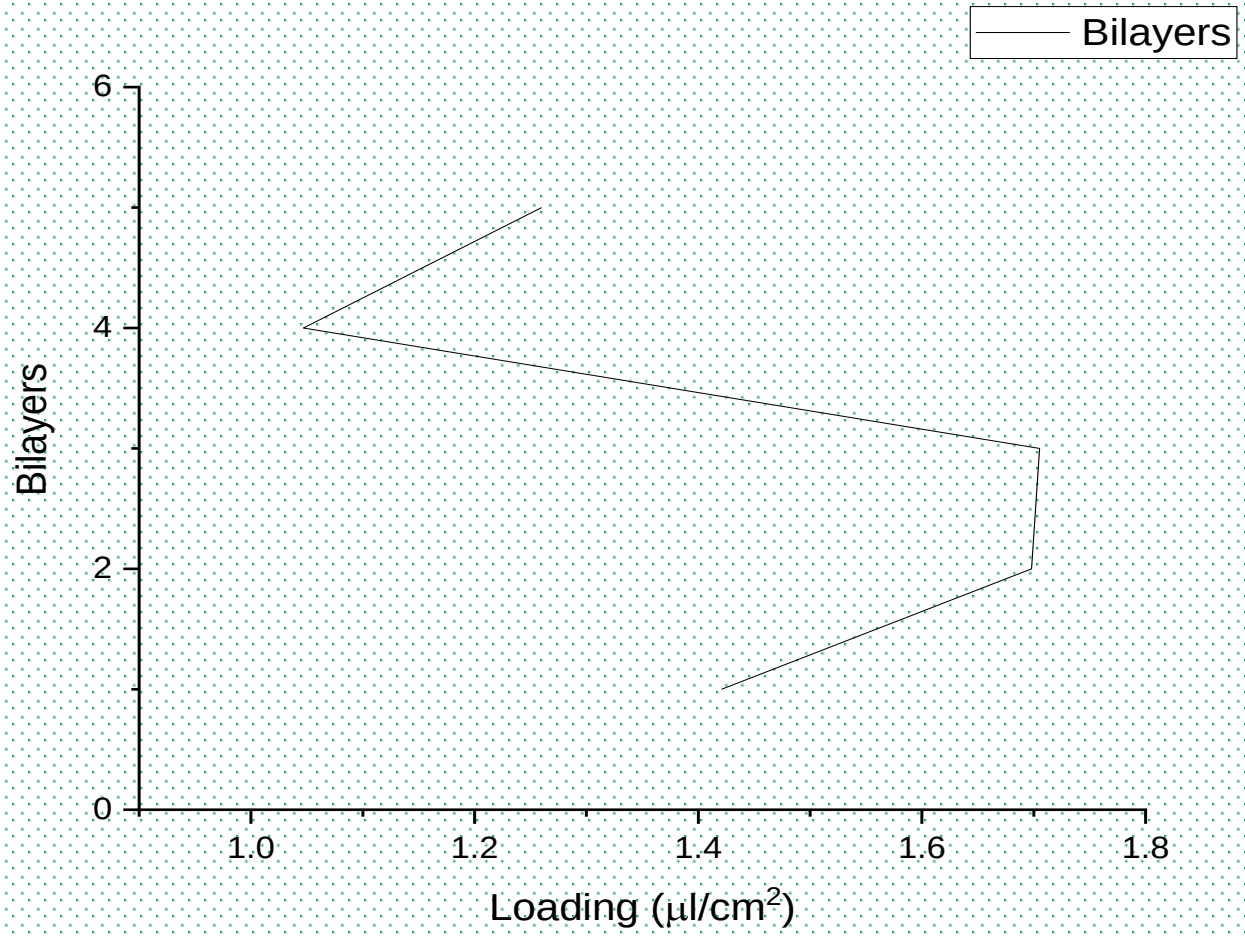
Since there is an absence of continuous film the printing process was stopped with 3rd bilayer and the reason for this instability was analyzed.

Contact angle and loading measurements:

Observations:

a.)Loading measurements:

Bilayers	Loading (µl/cm²)
1	1.4208
2	1.698
3	1.7053
4	1.047
5	1.26

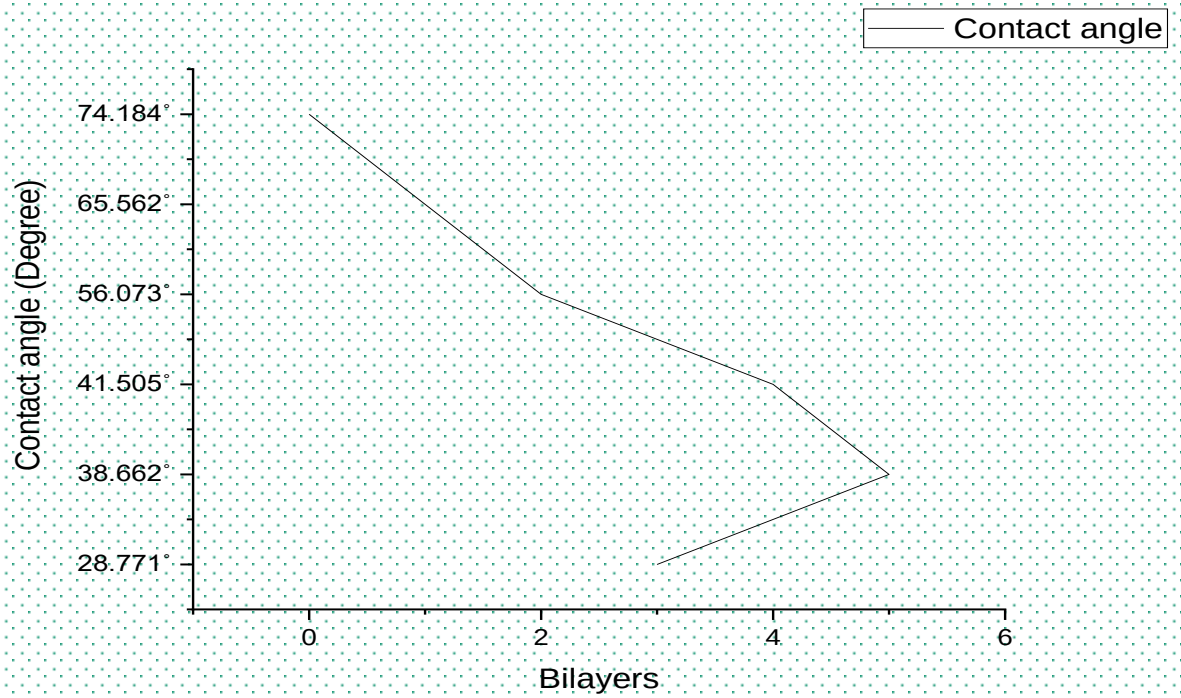


Contact angle and loading measurements:

Observations:

b.)Contact angle measurements:

Bilayers	Contact angle
Untreated PET	75.184°
1	65.562°
2	56.073°
3	28.771°
4	41.505°
5	38.662°



- **Inference:**

From, the contact angle & Loading measurements, due observed abnormalities it was hypothesized that there was no uniform PEL coating on the OHP substrate. So, the methodology of coating was changed

With varied bilayer coating:

Now the methodology of coating was changed instead of keeping all the samples in the beaker & keeping it in a incubator they were placed in a tray and each sides were exposed evenly in the PEL solutions(5 minutes each side).

- **Methodology 2:**

Using, this process a large amount of samples were been able to be PEL coated within a less amount of time.

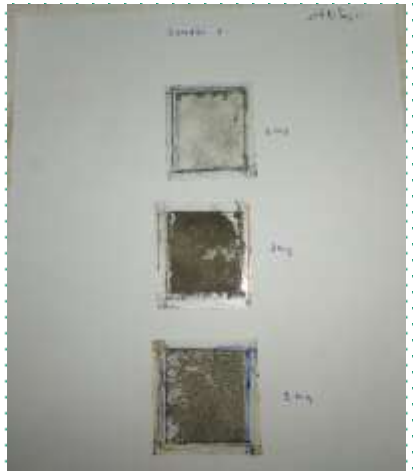
With varied bilayer coating:

Observations:

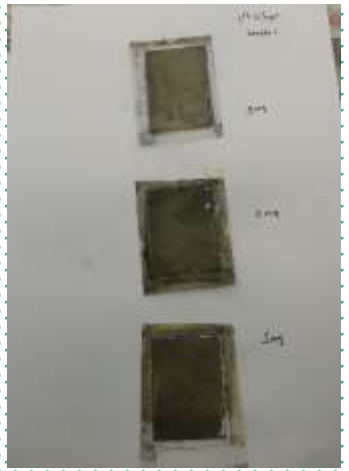
- 1st Bilayer:

2nd Bilayer:

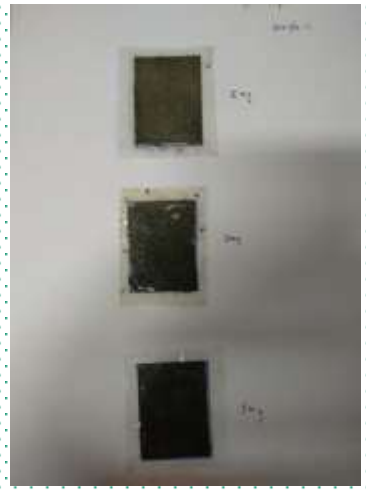
3rd Bilayer:

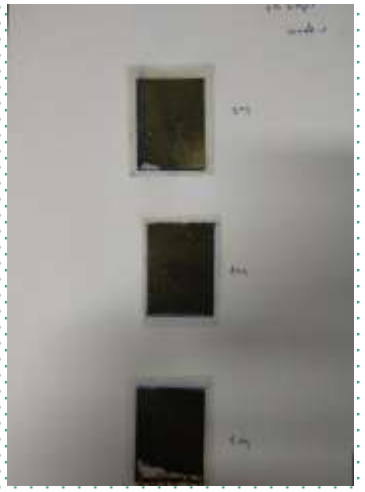


4th Bilayer:



5th Bilayer:





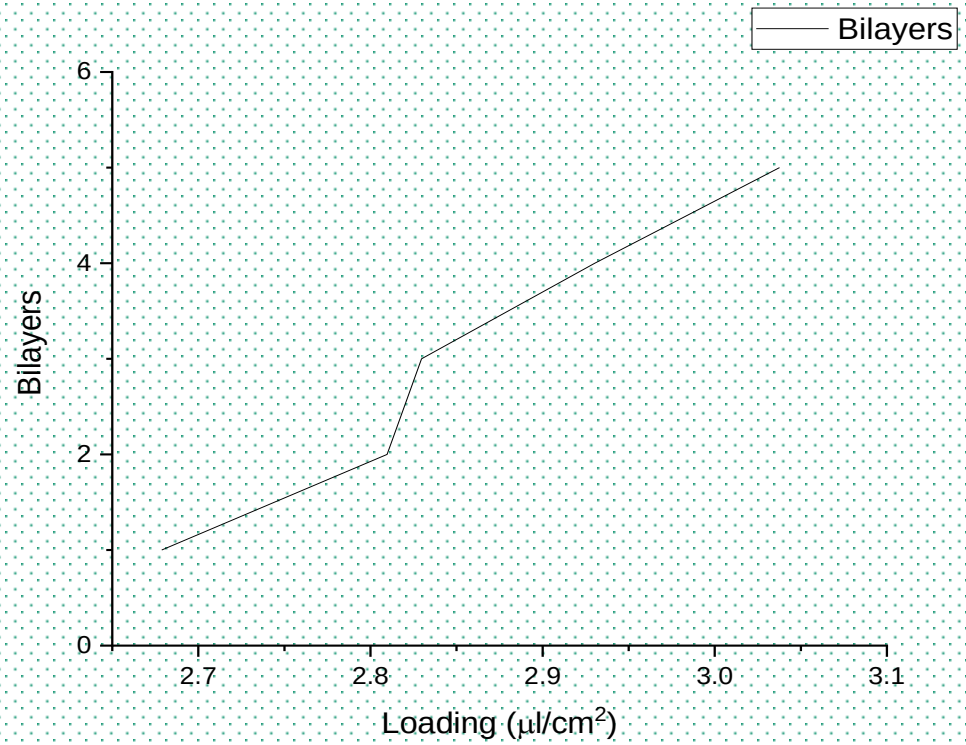
From, the above images it could be seen that this method of coating seems to show a much stable structure than the previous one.

Loading and Contact angle measurements:

Observations:

a.)Loading measurements:

Bilayers	Loading ($\mu l/cm^2$)
1	2.67875
2	2.809639
3	2.829617
4	2.930281
5	3.037662

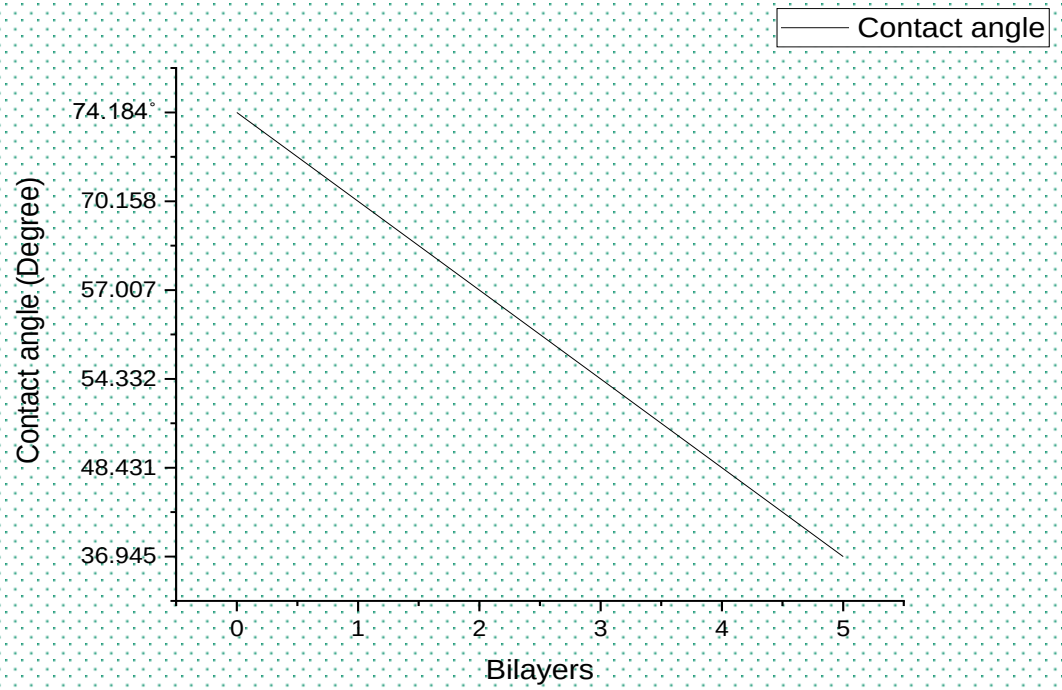


Loading and Contact angle measurements:

Observations:

b.)Contact angle measurements:

Bilayers	Contact angle
Untreated PET	75.184°
1	70.158
2	57.007
3	54.332
4	48.431
5	36.945



Resistance measurements:

Observations:

c.)Electrical resistance measurement:

	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

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. It's conductivity was checked with 2 probe method and found to be conductive.

Inferences:

- 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.

With varied bilayer coating on Nafion membrane:

- Now the printing substrate was changed to Nafion membrane and the printing process was continued with the similar concentrations.

- 1st Bilayer: 2nd Bilayer: 3rd Bilayer: 4th Bilayer: 5th Bilayer:



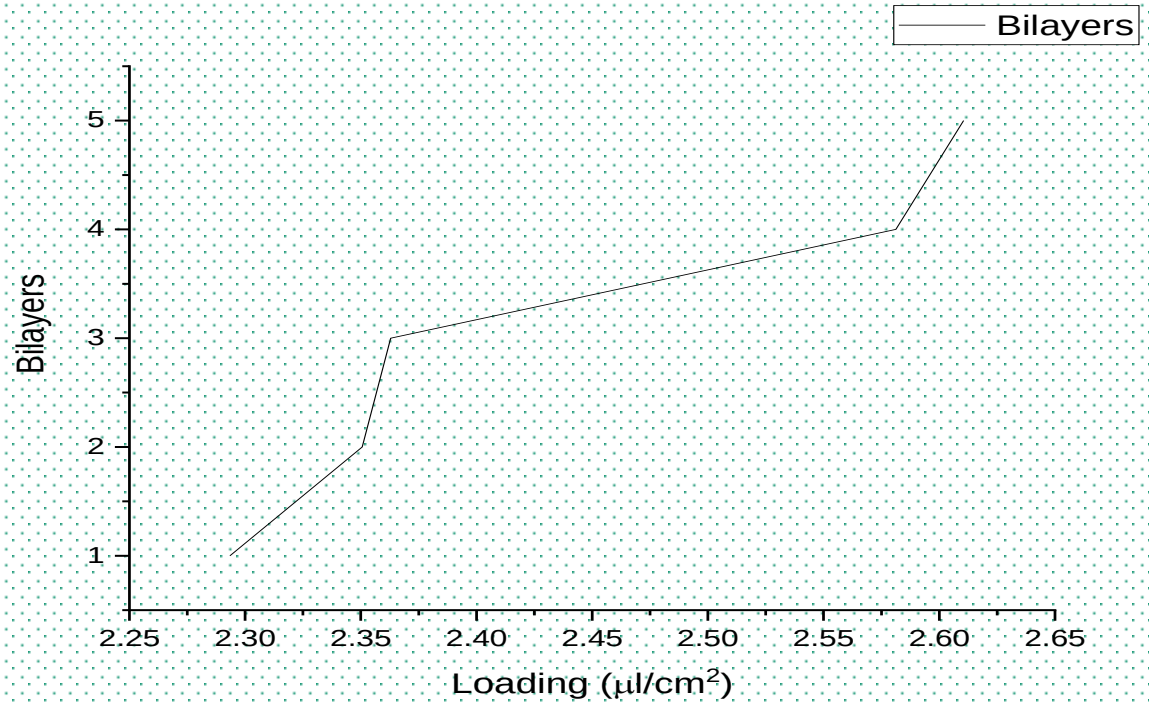


Loading and Resistance measurements:

Observations:

a.)Loading measurements:

Bilayers	Loading ($\mu l/cm^2$)
1	2.293388
2	2.350551
3	2.362948
4	2.581267
5	2.610537



As the bilayer coating on Nafion membrane increases, the cartridge loading also increased.

Loading and Resistance measurements:

Observations:

b.)Electrical resistance measurement:

	Resistance(ohms)					
	Sample-1			Sample-2		
Bilayers	1mg	2mg	3mg	1mg	2mg	3mg
5	53.6	16.3	3.5	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

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. It's conductivity was checked with 2 probe method and found to be conductive.

Inferences:

- The similar results of maximum loading , less PEL coating leaching happens was observed in Nafion.
- And it also showed the similar trend of increase in cartridge loading with increase in bilayer coating.
- Loading Increases, Resistance decreases.

Acid stability test:

- 15ml of 1N $HClO_4$(Perchloric acid) with a pH of less than 2 was used.
- AgNW printed Nafion samples of 3mg loading of Ag each and of different bilayers were kept in $HClO_4$ for 1 hour.

3rd Bilayer:

4th Bilayer:

5th Bilayer:

Acid stability test:

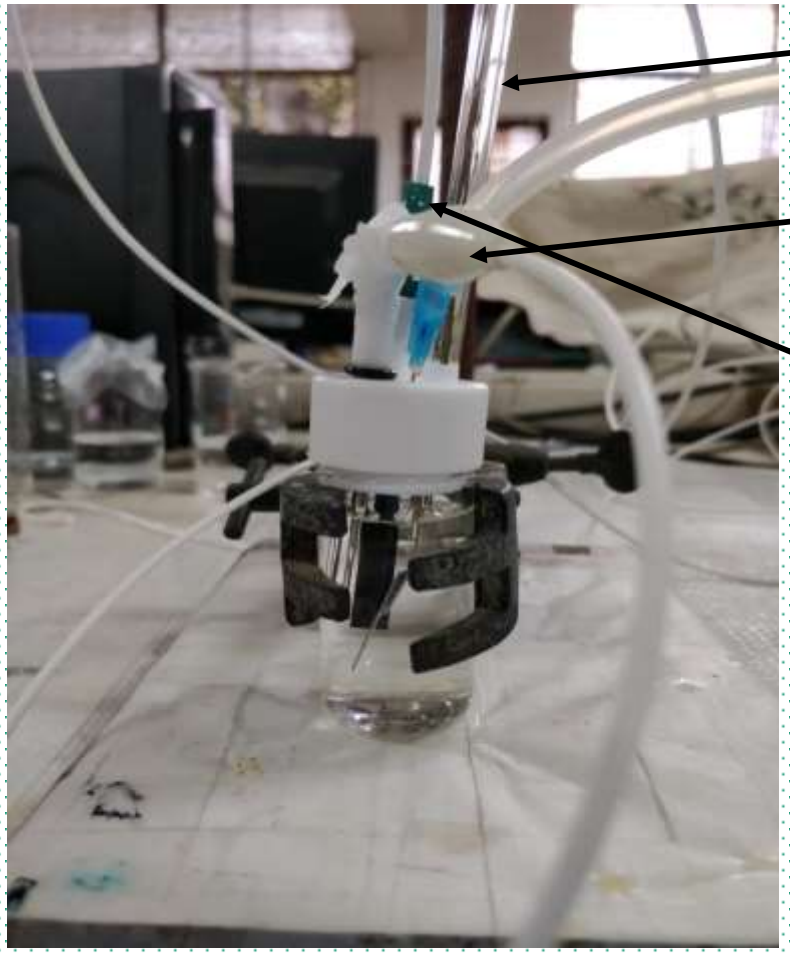
- **Resistance measurements:**

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

Inference:

- From the above table it can be seen that the AgNW structure appears to be stable in acidic solution for 5 bilayer PEL coating for 3mg Ag loading.
- So to have a high conductivity, high adhesion & high acid stability 5^{th} Bilayer with 3mg loading is chosen as the appropriate sample for Platinum Deposition.

Self-terminating Pt electrodeposition



Counter Electrode

Reference Electrode

Working Electrode

Anode (counter electrode):

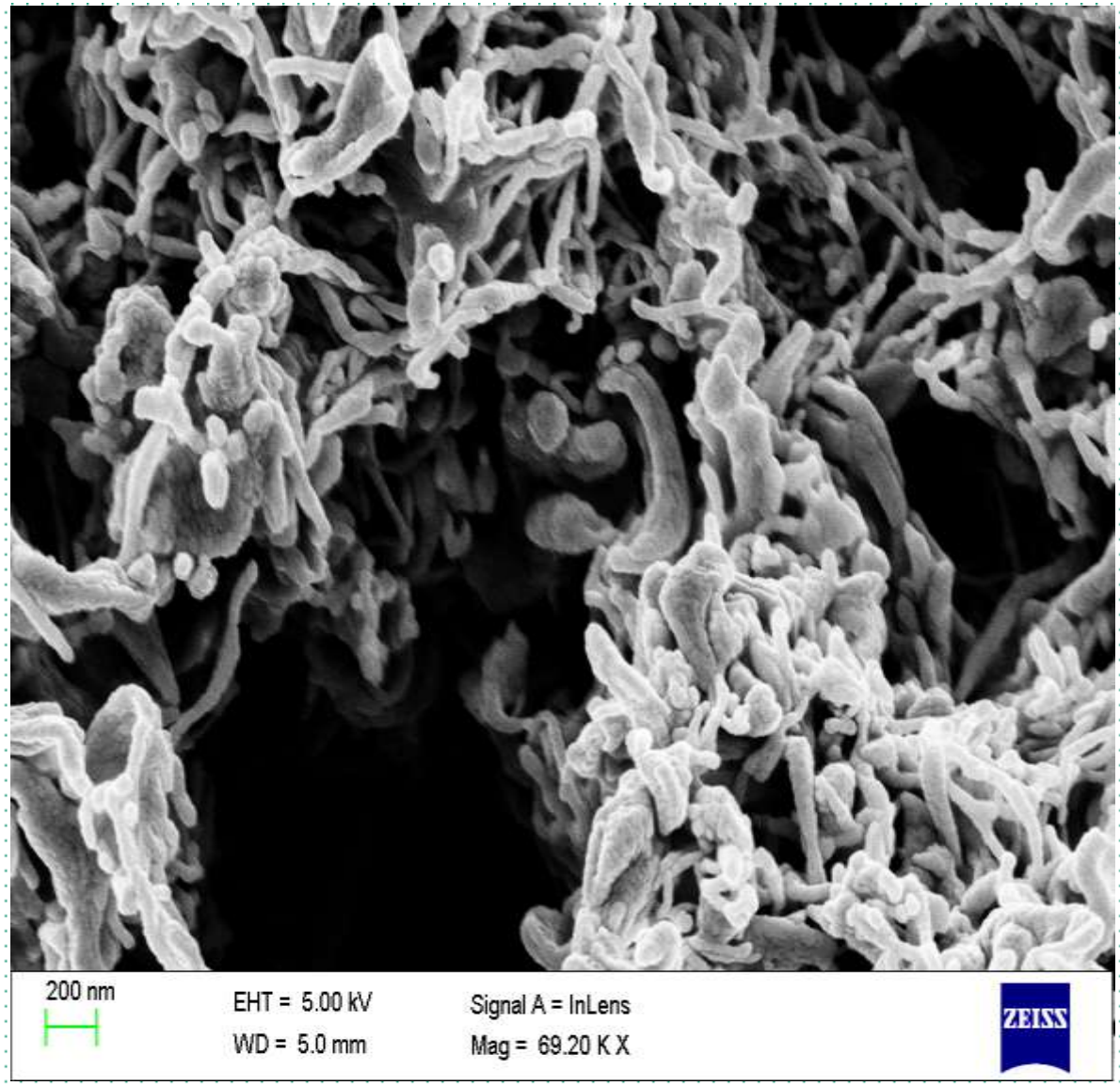
$$Pt \rightarrow Pt^{2+} + 2e^-$$

Cathode (working electrode):

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^-$$

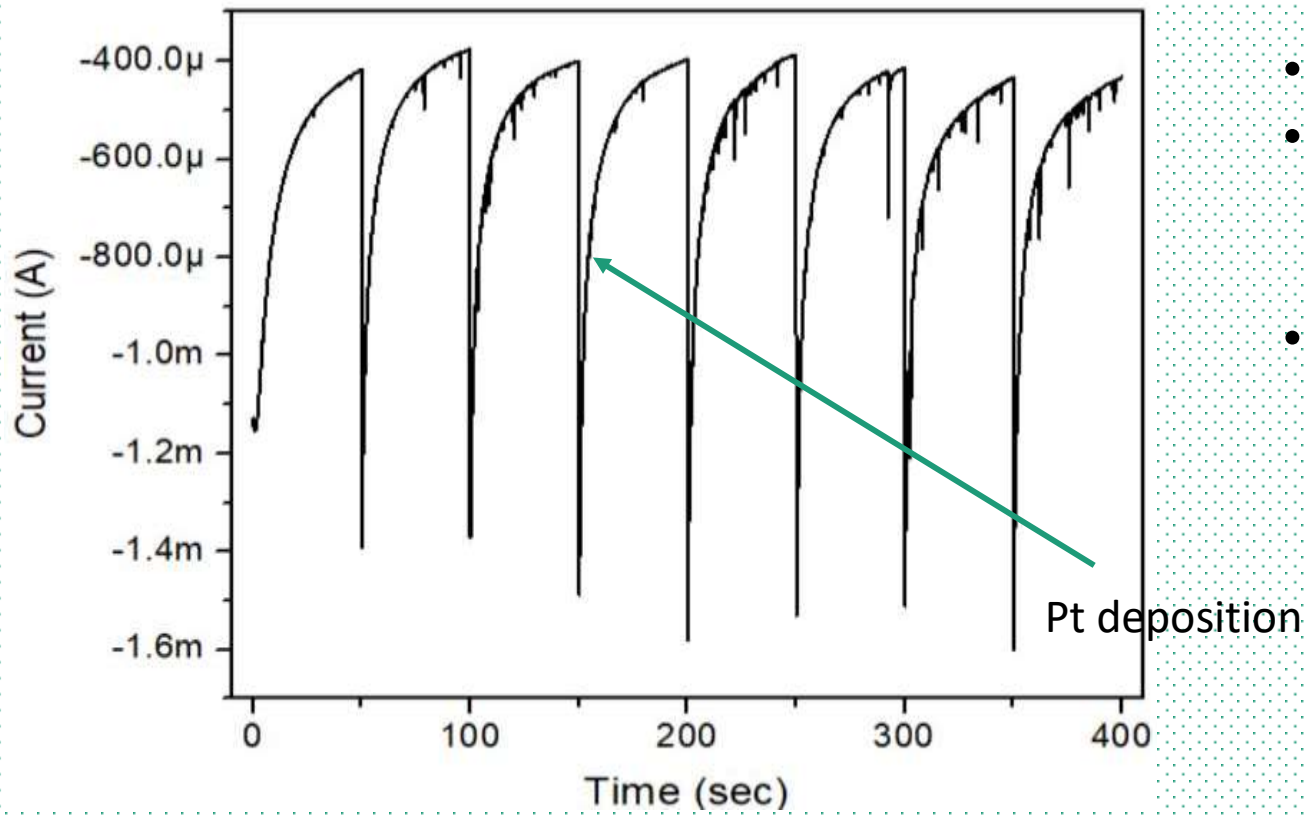
Pt gets reduced on the AgNW surface

SEM Characterization:

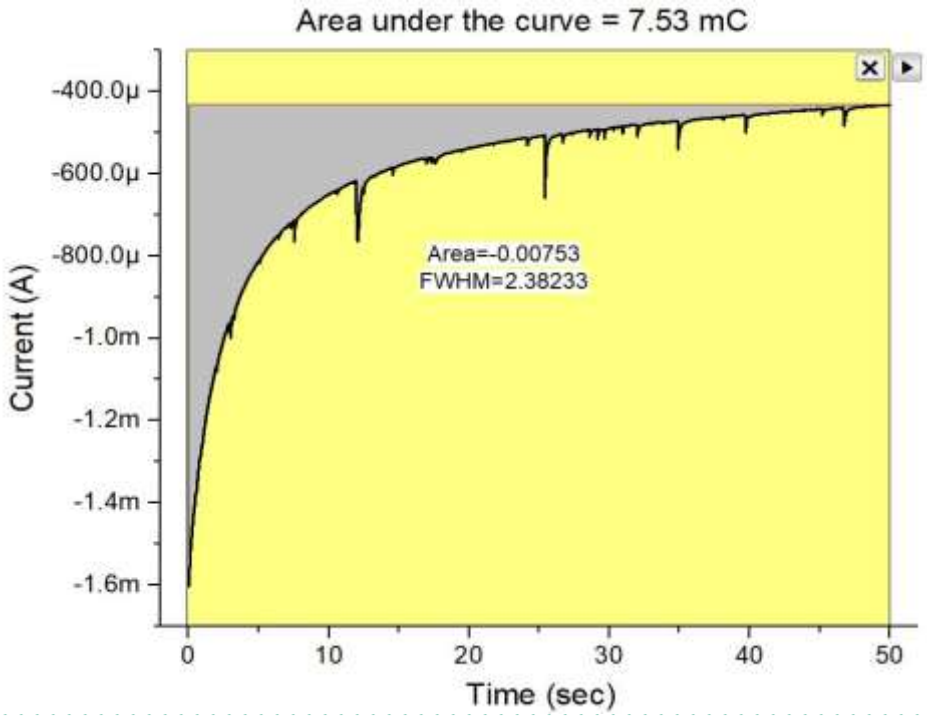


- FESEM of 3mg Ag loaded 5 bilayer sample without Pt deposition is show.
- Porous Ag Nanowire structure can be seen
- Resistance value before CA was 3.5Ω

Chronoamperometry:

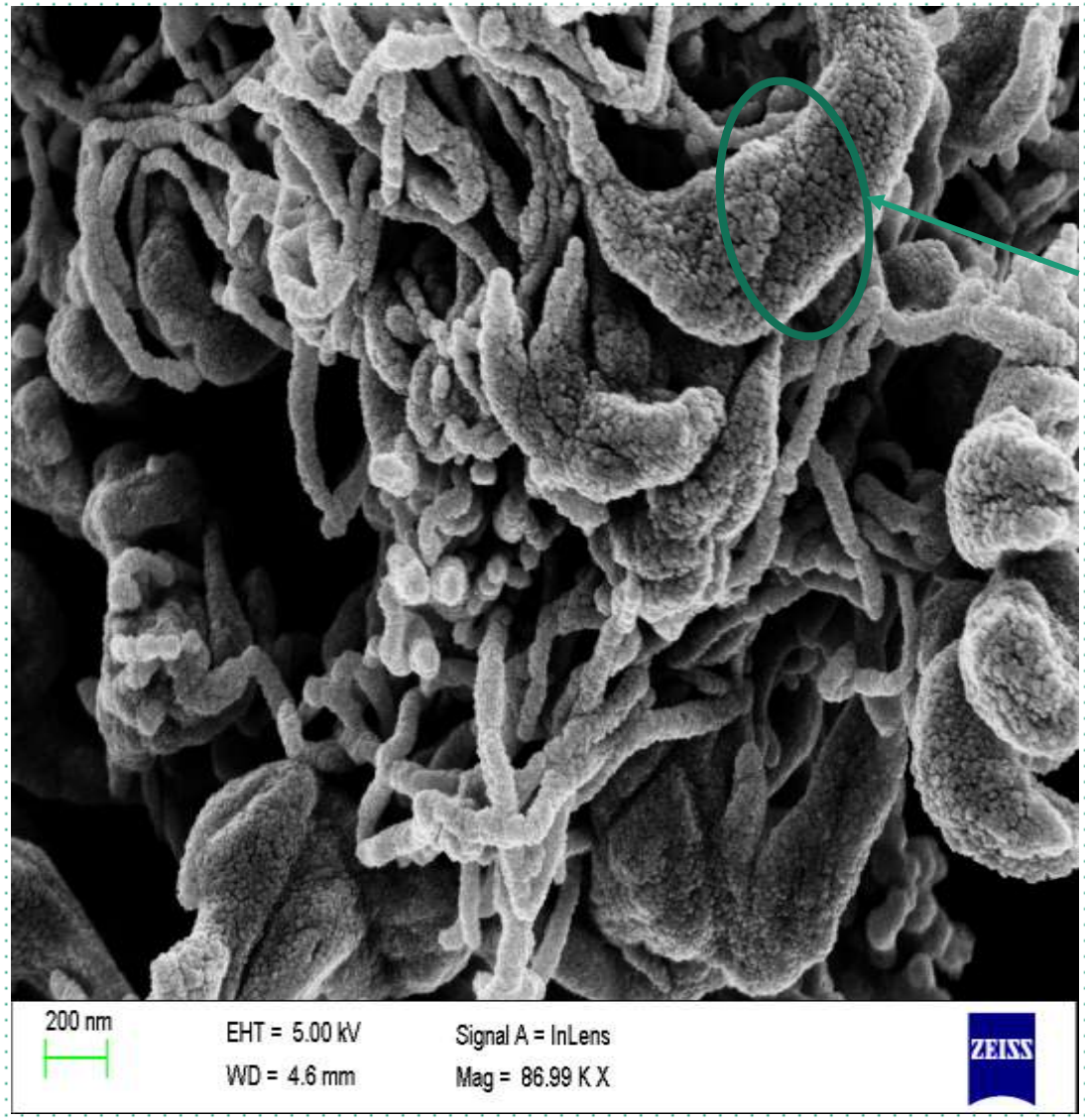


- -0.8V V/s Ag/AgCl electrode
- One way process of coating and the H_2 deposited is removed with water and blown with N_2
- 50 sec/cycle



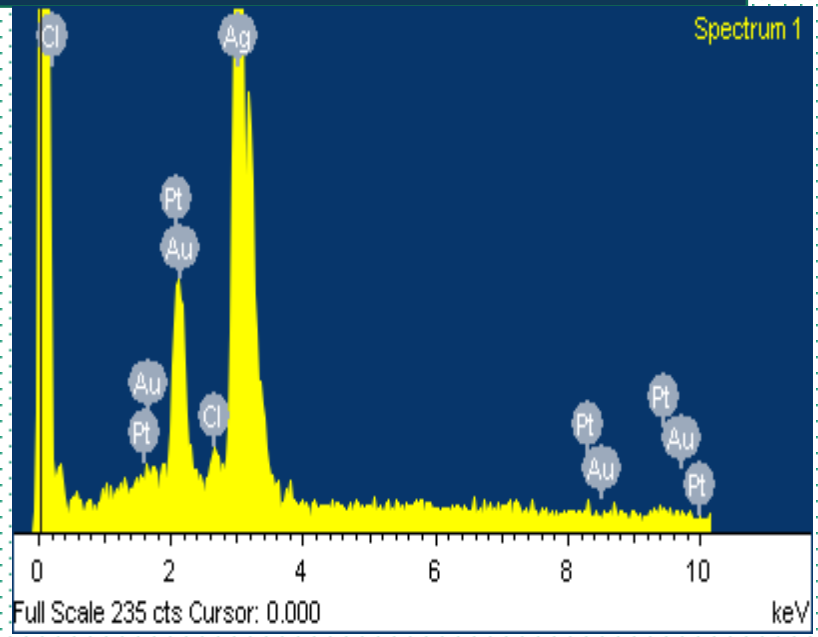
- Charge from I vs t curve, Faraday's law
- ~7.8µg/cm^2 i.e >10 µg/cm^2 per cycle

SEM Characterization:



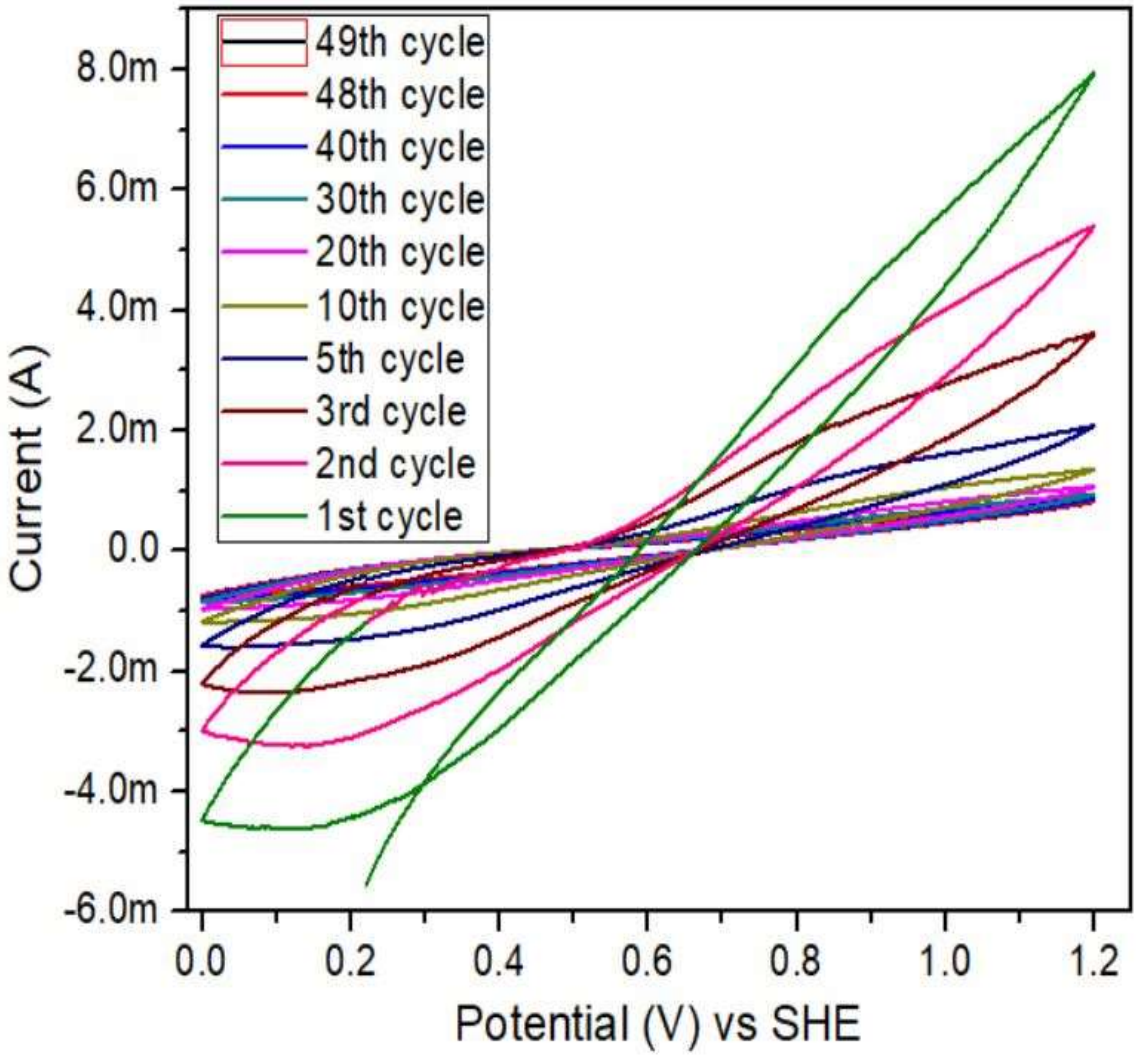
Granular Pt formation over the Ag percolating structure

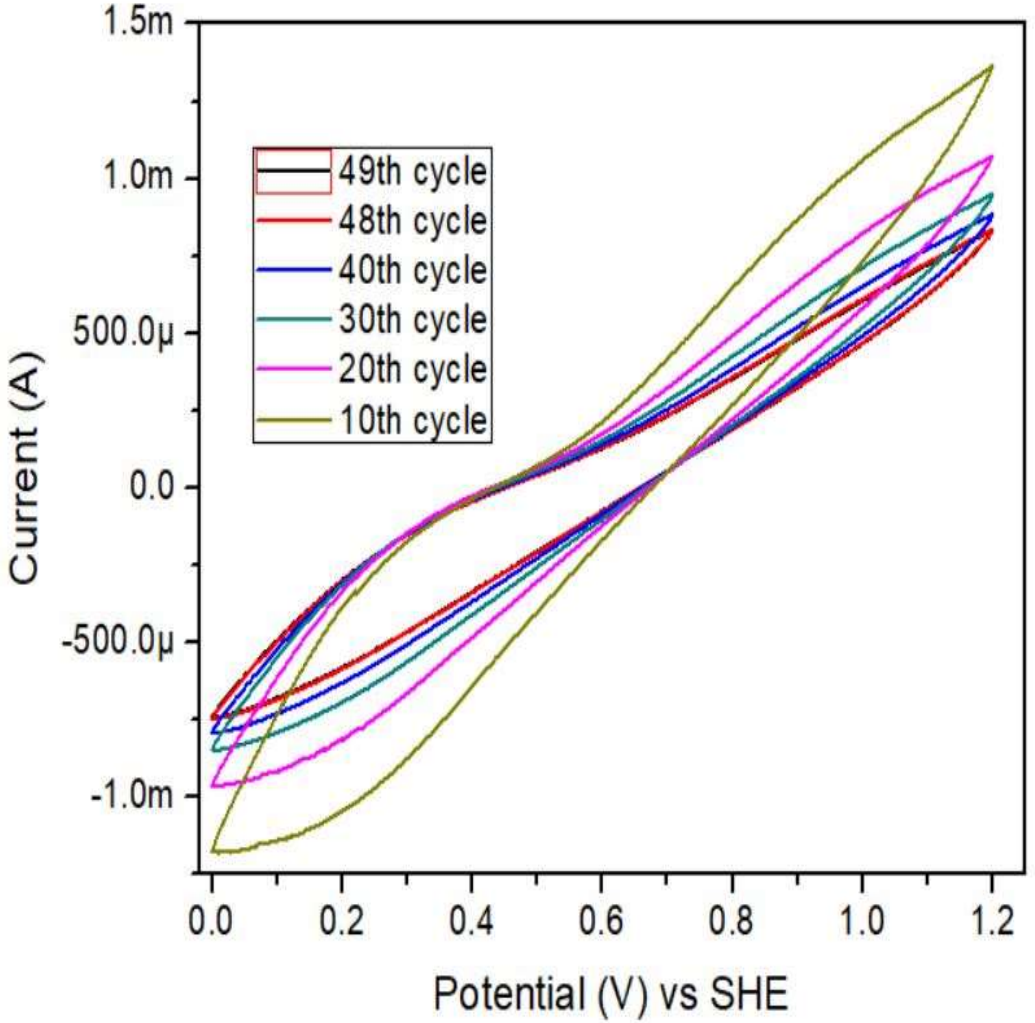
- $Pt/Ag = 0.08741\%$
- Nanowires beneath were intact,Pt deposition was uniform
- Pt was observed in SEM itself for 3mg/cm2 loading.
- Resistance after CA is 13.5Ω



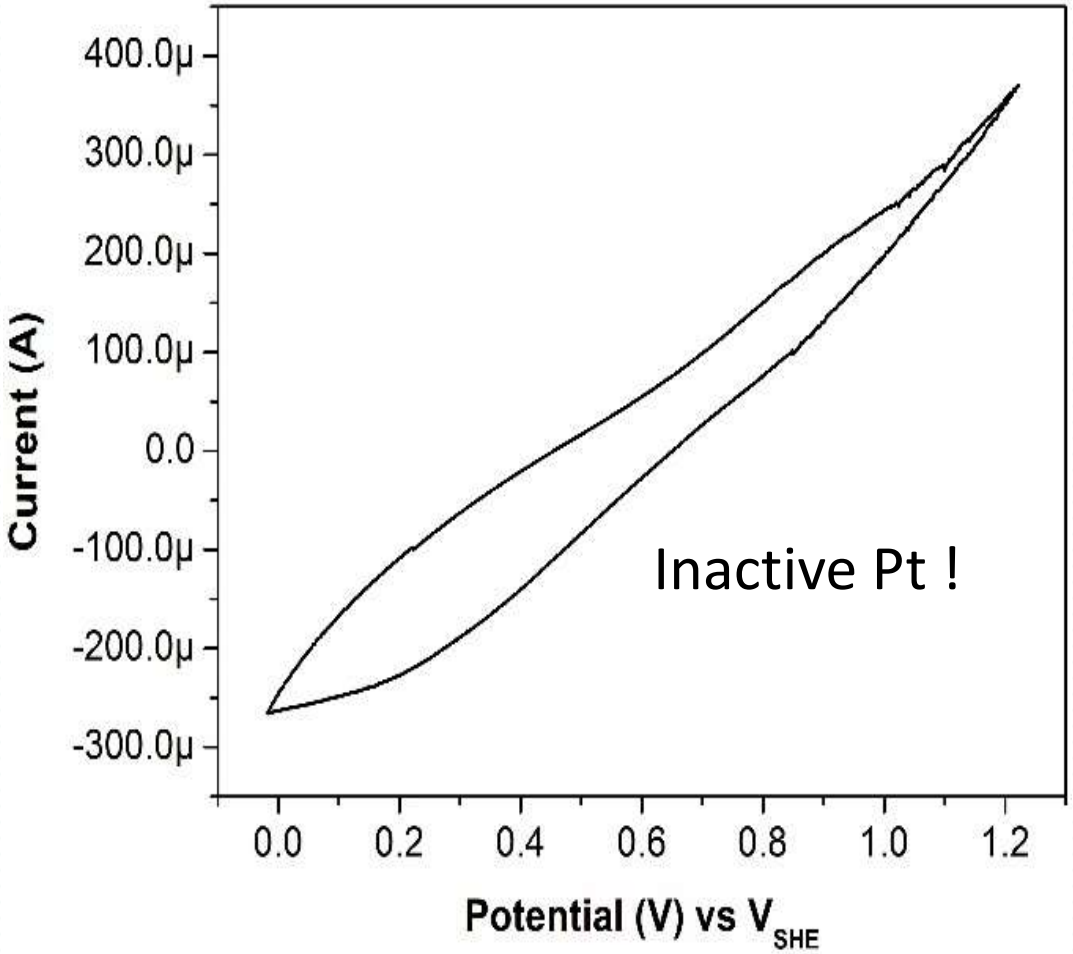
Element	Weight %	Atomic %
Cl K	0.26	0.87
Ag L	81.27	88.09
Pt M	13.00	7.79
Au M	5.46	3.24

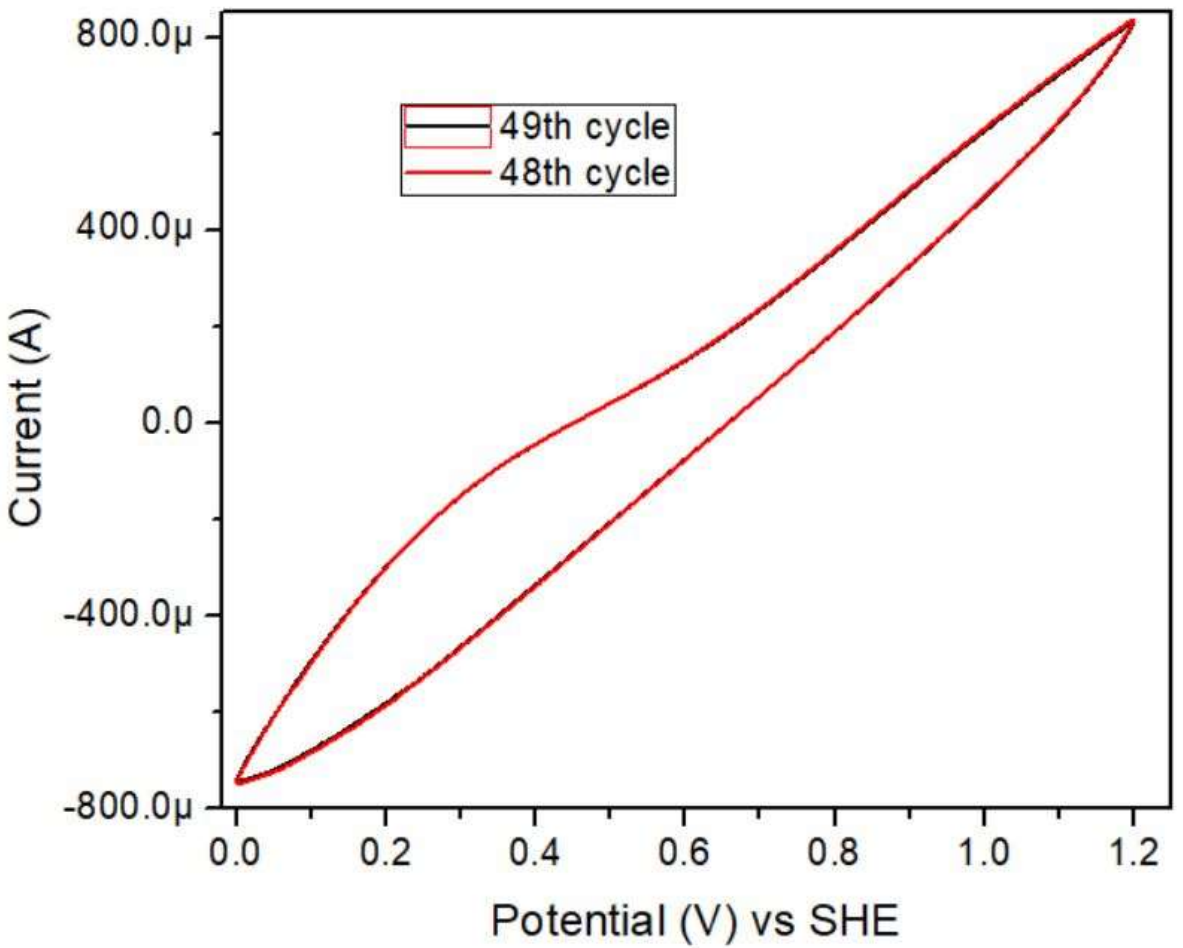
CV of platinum coated AgNW structure





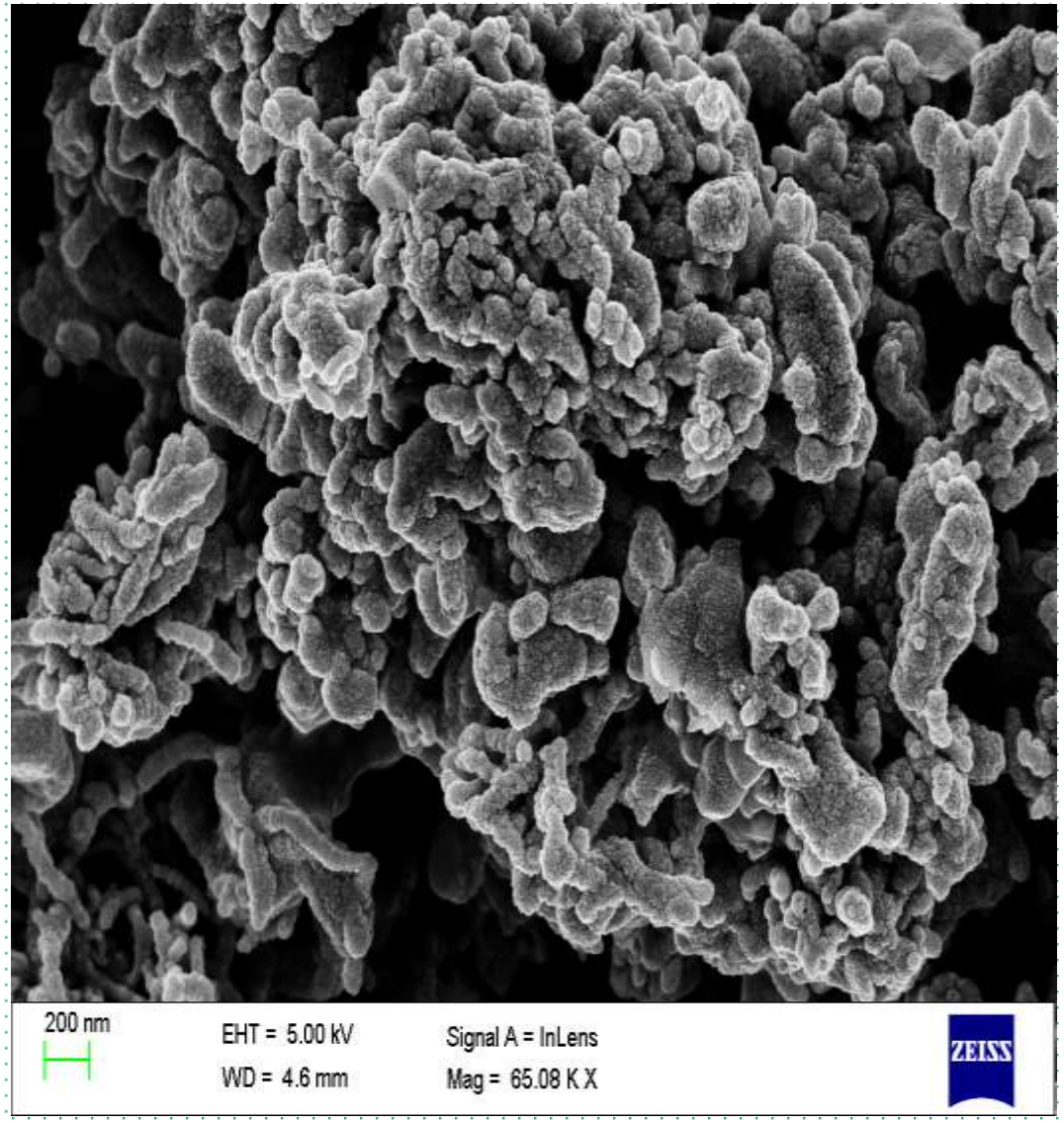
CV of platinum coated AgNW structure

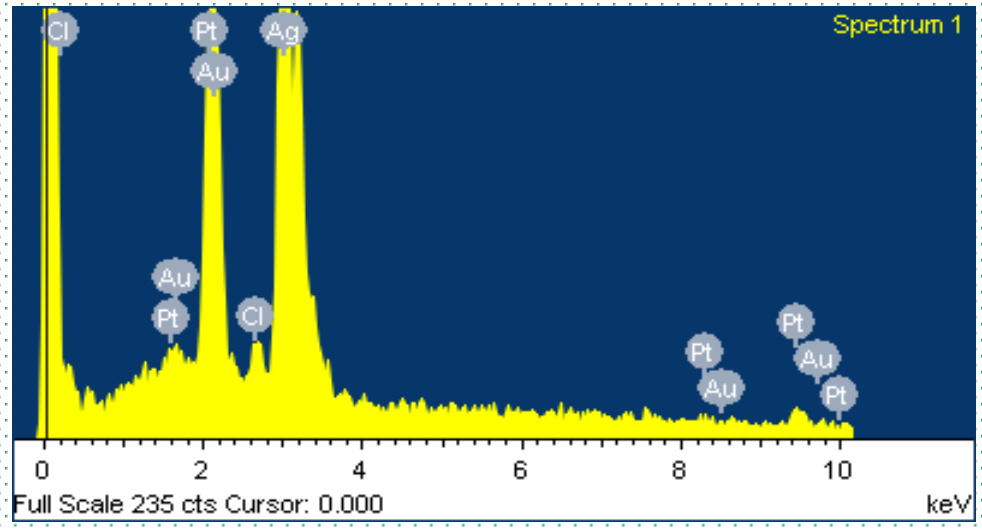




- The curve on the right side shows some amount of platinum is present at the end of 50th cycle
- Resistance after CV was 484.4Ω

SEM Characterization:





- **Inference**

An intact nanowire structure was absent.

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

Future scope:

- For, activation of platinum instead of 8 rounds of coating of Pt it can be increased to 16 rounds in 3mg/cm^2 loaded Ag Sample.
- Alternative methods of coating can be used to increase the stability of formation of AgNW on Nafion membrane(PVA+crosslinking agent)

Acknowledgements:

- Dr. Venugopal S
- Labmates
- Seniors

- Thank you!