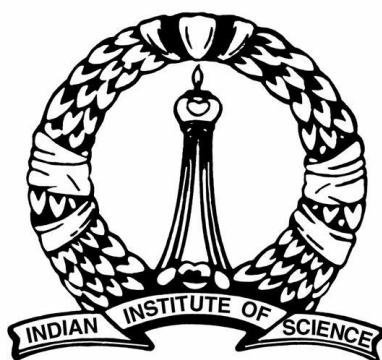


ELECTRODEPOSITION OF PLATINUM ON PAPER BASED SILVER NANOWIRES

SUMMER FELLOWSHIP PROGRAMME-2017

REPORT



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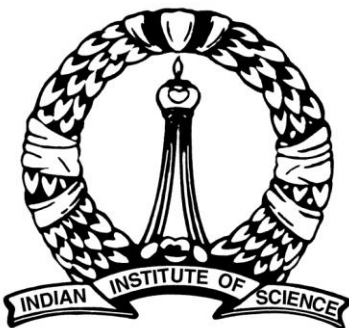
I express my deepest thanks to Ms. S Kaviya, my mentor, for her guidance, caring nature, invaluable suggestions and support that has enabled me to finish my mini project which was extremely valuable for me.

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CERTIFICATE

This is to certify that the work incorporated in this project entitled
“Electrodeposition of Platinum on Paper based Silver Nanowires”
has been carried out by **Shyamala B** (4th year, B Tech Chemical Engineering, SSN
College of Engineering, Kalavakkam) as a part of her Summer Fellowship
Programme from 12 June 2017 to 11 July 2017 at the **Department of Chemical
Engineering, Indian Institute of Science, Bangalore** under my supervision.

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INTRODUCTION:

Nanotechnology is the science that deals with metals at the scale of 1 billionth of a meter (i.e 10^{-9} m=1nm) and is also the study of manipulating matter at the atomic and molecular state .Metallic nano particles have different physical and chemical properties from bulk metals (e.g, lower melting point, higher specific surface area, specific magnetizations) properties that might prove attractive in various industrial applications.

Platinum nanoparticles have attracted considerable research interest because of their unique physical and chemical properties, many of which are advantageous in numerous research and industrial applications. Platinum nano particles are usually in the form of a suspension or colloid of nano particles of platinum in a fluid. Platinum nanoparticles are known to function as excellent catalysts for various chemical and electrochemical reactions such as in the *production of hydrogen from methane, oxygen reduction, formic acid oxidation* and the *hydrogen isotope exchange reaction between hydrogen gas and water using platinum catalyst* are exceedingly favorable to remove tritium from water in Nuclear industries¹.

For Such applications, the major requirements of catalyst are *large surface area and high dispersion of active sites*. The high surface area can be achieved by reducing the particle size of active catalyst to nanometer scale. The high dispersion requirement can be met by choosing proper support matrix for dispersion of catalyst material. Accordingly, effective processes for their fabrication are under intensive study². Various approaches have been employed for the fabrication of Pt nanoparticles, including

- the solution-phase method
- laser ablation method
- sonochemical method
- Reduction using bacteria cell as a hydrophilic Matrix
- Micro emulsion method
- Sol gel method
- Electrodeposition method .³⁻⁵

Compared with them, *Electrodeposition* has proven to be the most effective for arbitrarily controlling the morphology and size of the electrodeposited nanoparticles by suitably choosing the electrolysis conditions⁶⁻¹⁰. The electrochemical route is an effective procedure when compared with others which are complexity of the fabrication steps and impurity might be involved during the preparation.

Electrodeposition, a process where particle size distribution is highly controllable. Although when highly dispersed supports are used the electro crystallization show less homogeneous distribution of deposit. This is the reason of predominating chemical deposition techniques in the area of nanoparticles fabrication, but Pt electrodeposits also attract attention.

The deposition of two-dimensional (2D) Pt layers, which are also of interest in thin-film electronics and magnetic materials, is nontrivial because of the step-edge barrier to interlayer transport that results in roughening or 3D mound formation. Narrow size distributions of nano particles dispersed onto smooth, non-catalytic surfaces are great interest in various applications especially in the catalytic activity of platinum (Pt) towards reactions of interest in fuel cell systems.

However, Pt is expensive and the limited world supply of Platinum poses serious problems to widespread commercialization of fuel cell technology¹¹. Thus, research efforts in the development of cathode electro catalysts have been focused on decreasing the Pt content or replacing it with less expensive materials while maintaining high *Oxygen Reduction Reaction (ORR)* activity. Direct electrochemical reduction of Platinum ions on a support is a relatively convenient way to fabricate nanoparticle based electrodes. There are some reports in the literature on the preparation of supported Platinum nanoparticles via the electro deposition method¹²⁻¹⁴.

In this work, Silver Nanowire was printed on the paper using inkjet printing and it was used as a working electrode for electrodeposition process. Subsequently, Platinum Nanoparticles were electrodeposited on the silver nano wire. Its kinetics was studied by performing Linear Sweep Voltammetry using CH Instrument and the Platinum deposited silver nanowire was used for the cyclic voltammetry test of the standard ferrocyanide redox couple.

MATERIALS USED:

1. CHEMICALS:

- Potassium hexachloroplatinate
- Sodium Chloride
- Sulphuric acid
- Silver Nitrate
- Potassium Bromide
- Isopropyl alcohol
- Ethanol
- Sodium Sulphite
- Sodium hypochlorite
- Metol
- Quinol
- Borax
- Deionized water
- Potassium Ferrocyanide
- Potassium Nitrate
- Sodium hydroxide

2. APPARATUS:

- HP Inkjet Printer
- HP Black ink cartridge
- Halogen Lamp (Crompton greaves J240 V 500 W RTS,9500 lumens)
- Laminar hood (Esco)
- Sonicator (Bransonic ® Ultrasonic Cleaner)
- Syringe filter (Millex ® GV Filter Unit)
- Electrochemical Analyser (CH Instrument 608D)
- 4 Point meter (RCHEK-model RC2175)
- Hot Air Oven
- pH paper

- Glass wares
- Electrodes
- Crocodile clips
- Wires
- Cellophane tape

3. SOFTWARES:

- Microsoft Office Power Point 2013
- CHI 608D

SYNTHESIS OF PAPER BASED SILVER NANO WIRE:

PREPARATION OF SOLUTION:

All the chemicals were used were received from SDFCL, Fisher Scientific and Merck Chemicals which of high purity. All the solutions were prepared using DI water. 0.5M AgNO₃ and 1M KX solutions were prepared to print on paper. KX is a mixture of KBr and KI in the ratio 95: 5 KI was added to enhance the photosensitivity¹¹. The molar ratio of AgNO₃ to KX is always 1:2, to ensure complete conversion of AgX on paper. 3 layers of AgNO₃ and KX were printed to increase the conductivity of the silver nanowire. The developer solution was prepared by dissolving 0.2g of Metol, 10g of Sodium Sulphite, 0.5g of Quinol and 0.2g of Borax in 100ml of deionized water.

EXPERIMENTAL METHODS:

An inkjet printer was used to print the salt solutions on paper (A4 copier paper, 80 gsm). Three separate ink cartridges were used to print the different solutions. The black ink cartridge was opened and the sponge holding the black ink was removed. The cartridge was washed under the running tap and finally with DI water. Then the cartridge was used to print DI water and free prints for rough patterns were made on the paper surface to make sure it is printing properly and no black ink is left in the cartridge

The loading of the cartridge was found out by weighing the cartridge before and immediately after printing with DI water. This was repeated for five printings and the average of difference in their weights was noted. Knowing the density of water, the volume to be used per print could be found out. The loading of AgNO₃ was found to be 1.188mg/cm².

In this work, print-expose-develop process was followed. Twelve rectangle of (3x0.5 inch) each were drawn on Microsoft Office PowerPoint 2013 and printed alternatively with 0.5M AgNO₃ and 1M KX for six times. The reducing agent KX was printed on paper at first because it enhances the conductivity¹¹. The number of printings was increased to ensure uniform printing of the solutions on the paper and to increase the conductivity of silver on the printed area. As a

result of alternate printings, AgX layers were formed on the paper. This is identified by the greenish tint on the printed surface. The paper should be dried properly between each print. Printing on wet paper may block the print head and lead to cartridge failure.

After printing, the pattern was exposed under halogen lamp for 15 minutes. This leads to the formation of Ag clusters on paper. It is then dipped for 10 minutes in the developer solution, which is a source of electrons to reduce Ag ions¹¹. These ions on reduction change its lattice structure by breaking the clusters and forming Ag nanowires on paper. The color of the printed area was green and greenish brown after exposure to halogen lamp and development respectively. Developing the solution immediately after exposure showed higher conductivity compared to the exposed prints which were developed after few days. The developed print was then washed in DI water to remove the developer Solution from the surface of paper. It was put in a laminar hood for complete drying. The resistance value of one sample was measured using the four-point meter, which was found to be $35\Omega/\text{cm}^2$.

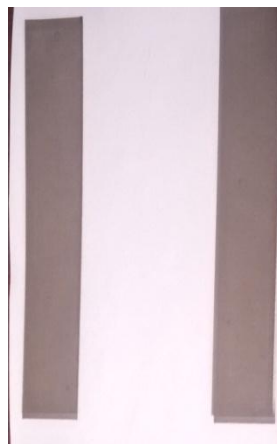


Figure 1: After development of the Ag nanowires

INSTRUMENTATION:

ELECTROCHEMICAL ANALYSER (CH INSTRUMENT):

The instrument is controlled by an external PC under Windows environment. The instrument provides many powerful functions, such as file handling, experimental control, graphics, data analyses, and digital simulation. Some of the unique features include macro command, *working electrode conditioning*, color, legend and font selection, data interpolation, visual baseline correction, data point removing, visual data point modification, signal averaging, Fourier spectrum, and equations relating to electrochemical techniques.

The instrument will be controlled by an IBM PC with Windows 95/98/NT/Me/2000/XP operating system. A free serial port or a USB port is required for communication between the instrument and the computer

Cyclic Voltammetry and *Linear Sweep Voltammetry* were performed using an Electrochemical Analyzer and the results were discussed.

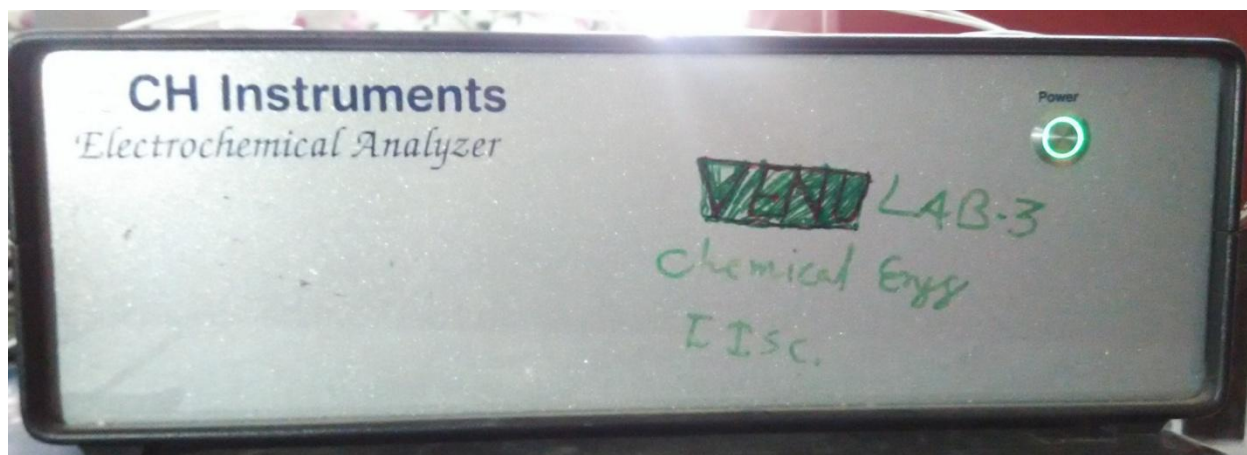


Figure 2: Electrochemical Analyzer

DEPOSITION OF PLATINUM ON SILVER NANOWIRE:

EXPERIMENTAL SETUP:



Figure 3: Electrochemical Cell

- **Working Electrode:** Paper based Silver Nanowire
- **Counter Electrode:** Platinum Wire
- **Reference Electrode:** Saturated Calomel Electrode(SCE)
- **Electrolyte:** 3mmol/L of Potassiumhexachloroplatinate(K_2PtCl_6)
0.5mol/L of Sodium Chloride (NaCl)
- **pH:** 4

PREPARATION OF ELECTROLYTE:

14.5797 mg of K_2PtCl_6 and 292.2mg of NaCl were measured using weighing machine and dissolved completely in 30ml of deionized water using Sonicator and the solution was transferred into 100ml beaker. 3 drops of 98% AR Sulphuric acid was taken using micropipette and poured into 10 ml of deionized water and the solution was shaken well. 3 drops of acid solution was poured into the electrolyte solution .pH of the solution was checked using pH meter. All the chemicals were of analytical grade and used without further purification. The same grade of water was used for rinsing and cleaning activities.

EXPERIMENTAL METHOD:

The electrochemical experiment was performed in a three-electrode cell arrangement. Three relevant leads of the CH instruments such as Red, Green and white were connected to Platinum Wire (Counter Electrode), Paper based Silver Nanowire(Working Electrode) and Saturated Calomel Electrode (Reference electrode) respectively.

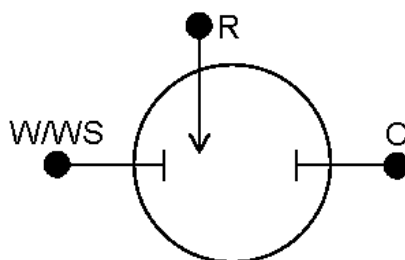


Figure 4: Electrode Cell Setup

These three electrode were mounted inside the 100ml beaker using Crocodile clips and Cellophane tape. All the electrodes were completely dipped into the Electrolyte Solution. Electrodeposition process was accomplished by scanning between a few ranges of voltage versus SCE at a suitable scan rate for suitable cycles in an electrolytic bath containing Pt salt. ED is widely used with different strategies/methodologies, such as Linear Sweep voltammetry and Cyclic Voltammetry. *Linear Sweep Voltammetric measurements* were carried out to clarify the electrochemistry of the $[\text{PtCl}_6]^{2-}$ -Pt redox system. The electrochemical characterization of the

deposited platinum nanoparticles was performed by *cyclic voltammetry* in Ferrocyanide Solution. In this case, the potential was swept between -0.8 and 0.4 V at the rate of 2 mV/s.

RESULTS AND DISCUSSION:

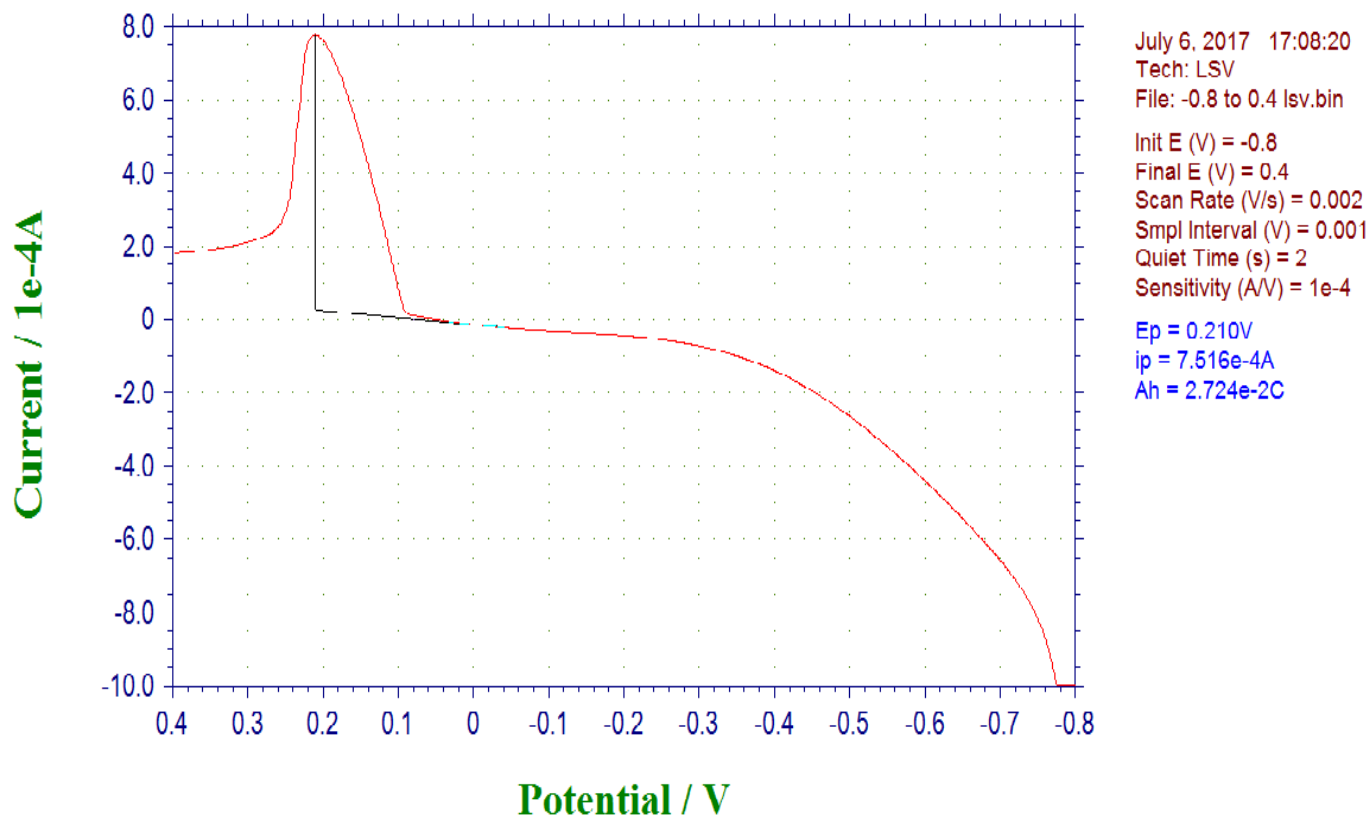
KINETIC STUDY OF $[\text{PtCl}_6]^{2-}$ REDUCTION:

LINEAR SWEEP VOLTAMMETRY TEST:

Linear Sweep Voltammetry (LSV) was employed to study the reduction kinetics of $[\text{PtCl}_6]^{2-}$ from solutions consisting of 0.50 mol/L NaCl and 3mmol/L K_2PtCl_6 . The influence of pH, adjusted by NaOH additions, was examined in an electrochemical cell filled with 30ml electrolytic solution.

| | |
|----------------------------|------------------------------------|
| Initial E(V) | -0.8 |
| Final E(V) | 0.4 |
| Scan rate (V/s) | 0.002 |
| Sample Interval (V) | 0.001 |
| Quiet Time(sec) | 2 |
| Sensitivity (A/V) | 1e^{-4} |

Table 1: Parameters Used for Linear Sweep Voltammetry



Graph 1: Voltammetric measurement of Pt deposition from a NaCl-PtCl_6^{2-} Solution

Voltammetry in Graph 1 showed that the onset of Platinum deposition at 0.210V versus a Saturated Calomel Electrode followed by a substantial current rise to maximum at 0.210V. Beyond the peak, the deposition rate decreased smoothly as the mass transfer boundary layer thickness expanded. Drop in the current occurred when the potential moved to 0.261 V, eventually reached minimum near 0.4 V. The drop in Current above 0.261 V corresponded to the complete quenching of metal deposition

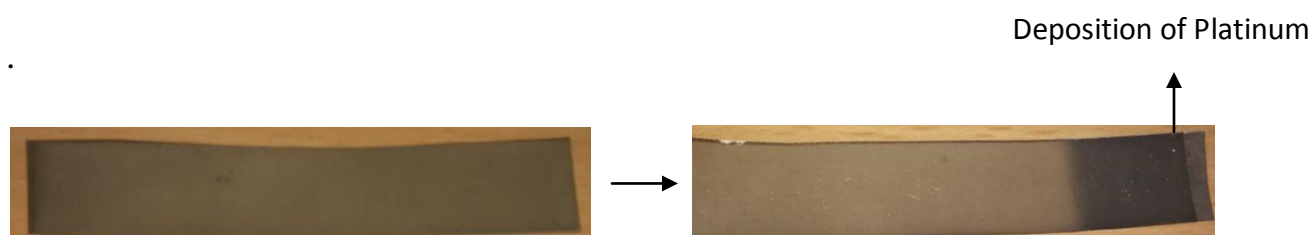


Figure 5: Paper based Silver Nanowire **before** and **after** Electrodeposition Process

The change in color of the silver nanowire revealed that the platinum ions were deposited on it.

CONDUCTIVITY TEST:

Before the deposition of Platinum on Paper based Silver nanowire, the resistance was $66 \Omega/\text{cm}^2$. After the electrodeposition process, the resistance of the nanowire was reached to $549 \Omega/\text{cm}^2$. This analytical results also confirm that Platinum was deposited on Paper based Silver nanowire.

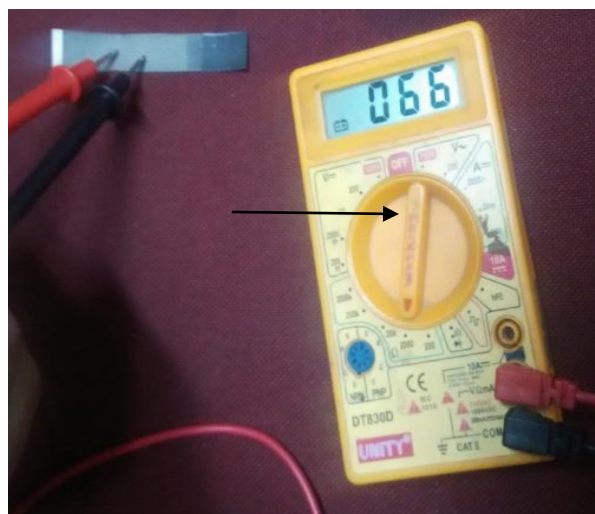


Figure 8: Resistance value of Silver nanowire **before** electrodeposition process



Figure 9 : Resistance value of Silver nanowire after electrodeposition process

CYCLIC VOLTAMMETRY TEST:

Cyclic voltammetry is the most versatile electro analytical technique for the study of electro active species, and it is widely used in industrial applications and academic research laboratories¹⁵. This technique was performed to study the potential of potassium ferrocyanide which undergoes redox reaction easily. The technique was performed for Platinum deposited Silver nanowire.

| | | | |
|------------------------|--------------|----------------------------|------------------------|
| Initial E(V) | -0.8 | Segment | 2 |
| Final E(V) | 0.4 | Sample interval (V) | 0.001 |
| Low E(V) | -0.8 | Quiet time (s) | 2 |
| Final E(V) | 0.4 | Init P/N | P |
| Scan rate (V/s) | 0.002 | Sensitivity (A/V) | 1e⁻⁴ |

Table 2: Parameters used for Cyclic Voltammetry

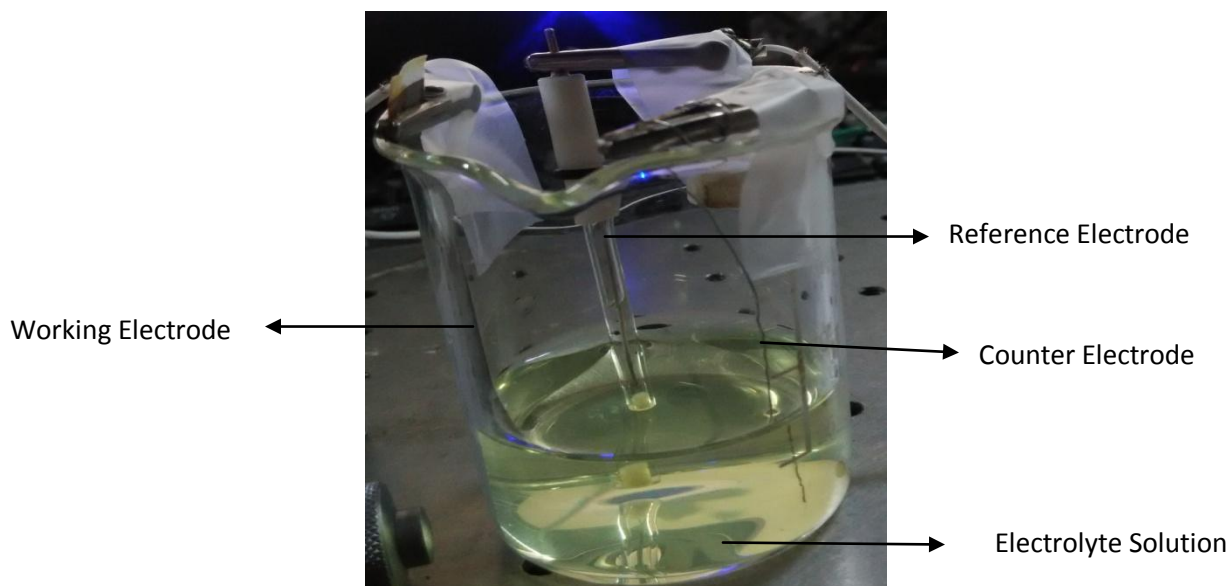
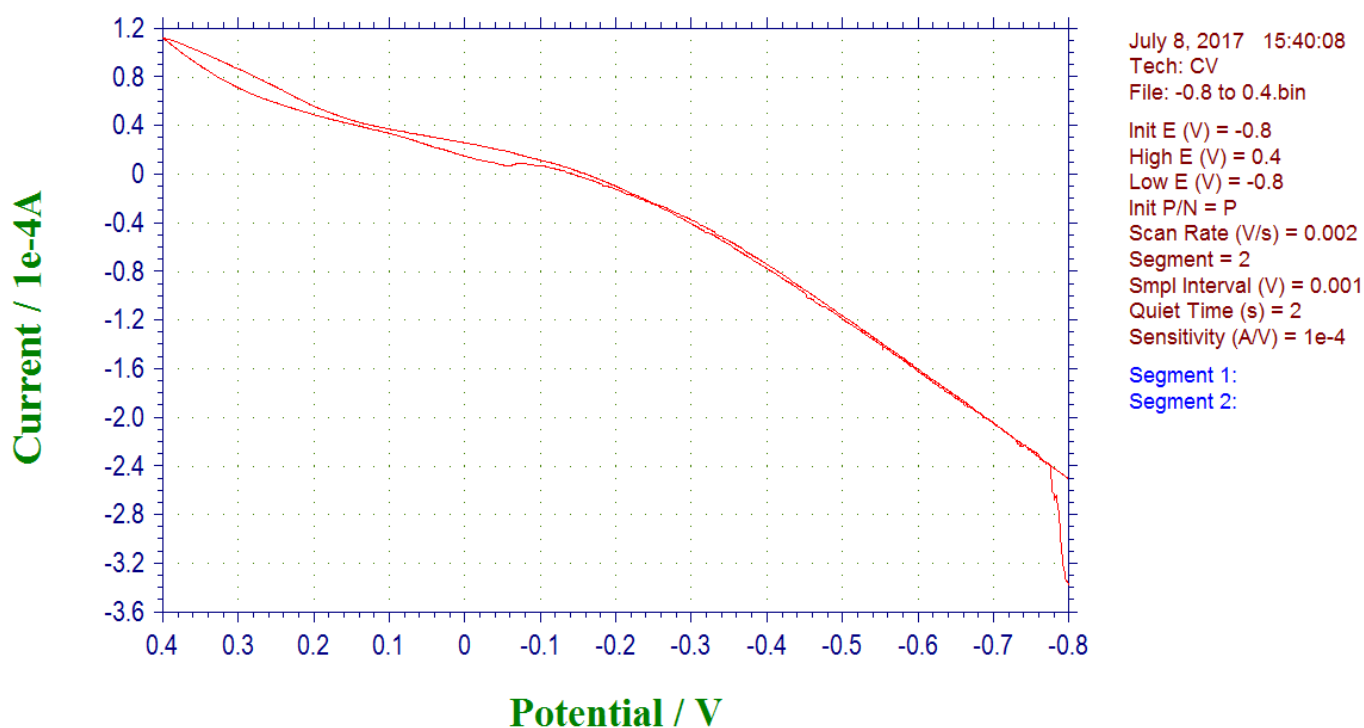


Figure 9: Electrochemical setup for Cyclic Voltammetry Studies

- **Working Electrode:** Platinum deposited Paper based Silver nanowire
- **Counter Electrode:** Platinum Wire
- **Reference Electrode:** Saturated Calomel Electrode(SCE)
- **Electrolyte:** 10mmol/L of Potassium ferrocyanide ($K_4[Fe(CN)_6]$)
1mol/L of Potassium nitrate (KNO_3)
- **pH:** 4

PREPARATION OF ELECTROLYTE:

63.3585 mg of $K_4[Fe(CN)_6]$ and 1516.548 mg of KNO_3 were measured using weighing machine and dissolved completely in 30ml of deionized water using Sonicator and the solution was transferred into 100ml beaker. 3 drops of 98% AR Sulphuric acid was taken using micropipette and poured into 10 ml of deionized water and the solution was shaken well. 3 drops of acid solution was poured into the electrolyte solution .pH of the solution was checked using pH meter.



Graph 2: Cyclic Voltammetric Studies of Potassium Ferrocyanide System

The Ferrocyanide redox system used in this study is one of the most extensively studied redox couples in electrochemistry and exhibits a heterogeneous electron transfer. Here Platinum deposited Silver nano wire displayed no redox peak, likely due to improper deposition of Platinum on Silver nanowire. Nevertheless, the current shown by Cyclic Voltammetry was higher than that of the current displayed by Linear Sweep Voltammetry indicating an electrical contact between Platinum and the Silver nanowire backing.

CHARACTERIZATION OF THE PLATINUM DEPOSITED SILVER NANOWIRE SURFACE MORPHOLOGY:

Scanning Electron Microscopy (SEM):

The Scanning Electron Microscopy uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimen. The signals that derive from electron-sample interaction reveal information about the sample including external morphology, chemical composition and crystalline structure and orientation of materials making up the sample¹⁶.

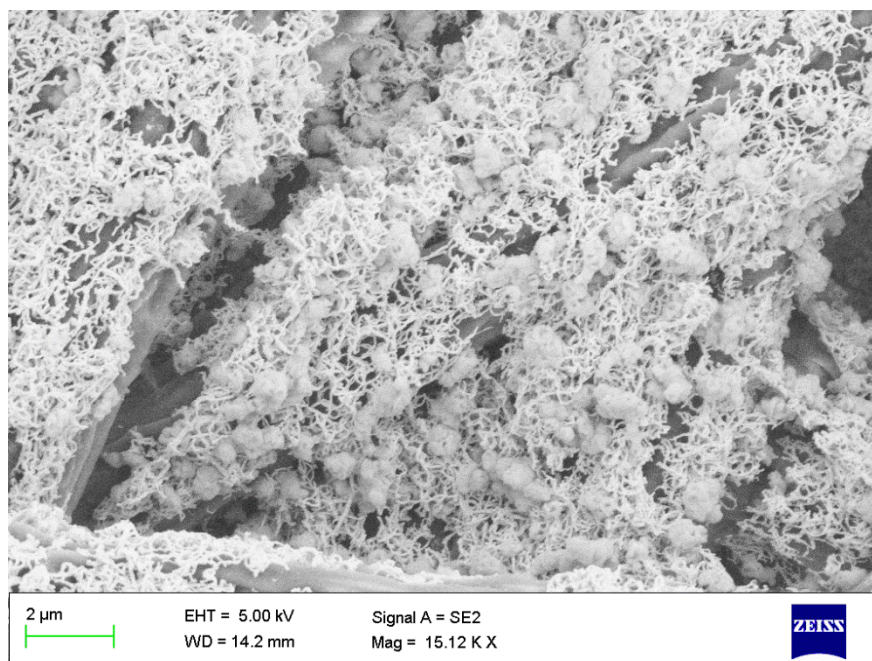


Figure 10: SEM images of Platinum particles deposited on Silver nanowire at Magnification of 15.12 K X

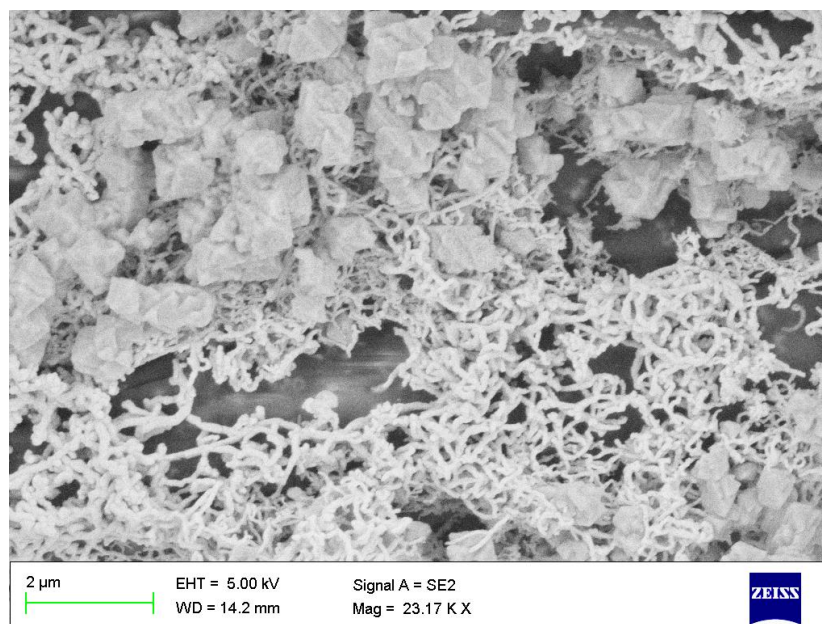


Figure 12: SEM images of Platinum nanoparticles

Morphological characteristics of the Pt-nanoparticles-deposited on Paper based Silver nanowire were studied by scanning electron microscopy (SEM).

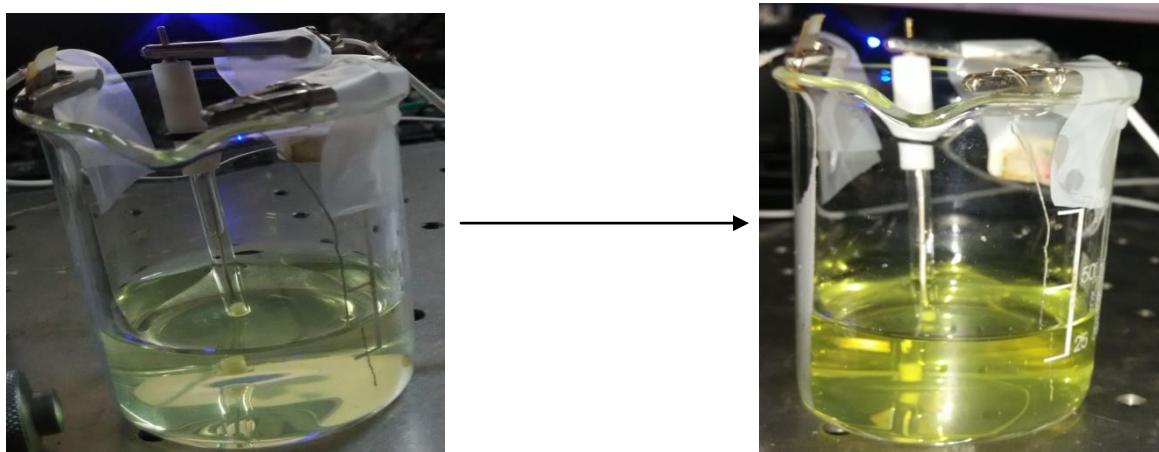
FUTURE STUDIES:

This present work demonstrates a new synthetic route toward Pt particles using a solid Pt ion precursor composed of K_2PtCl_6 . This novel method for Pt fabrication is electrochemically mediated, utilizing the direct reduction of a solid-state Pt precursor suspension coated on the surface of the Paper based Silver nanowire. In brief, it is possible to obtain very small Pt particles deposited onto Paper based nanowire. Platinum nanoparticles are in electrical contact with the nanowire, enabling the composite structure to be used as an electrode. This composite structure enables a new class of electrode materials and offers an excellent platform for various Fuel Cells and biosensing applications.

The platinum deposited nanowires can be used for both the electrode and the catalyst in Solid oxide fuel cells. It will act as a current collector to enhance the fuel cell performance.

CONCLUSION:

Platinum nanoparticles were electrodeposited on Paper based Silver nanowire from an aqueous electrolyte containing Potassium hexachloroplatinate by a Linear Sweep Voltammetry Method. The Platinum deposited nanowires were characterized by electrochemical means and by scanning electron microscopy. It was found that the particle size and distribution on the support were strongly dependant on scan rate. When Platinum deposited Silver nanowire was dipped into the Ferrocyanide Solution, It was found experimentally that the Platinum particles were not strongly adherent to the Silver nanowires. Since, color of the electrolyte solution was changed.



(a)

(b)

Figure 13: (a) Before Conducting Ferrocyanide test

(b) After Conducting Ferrocyanide test

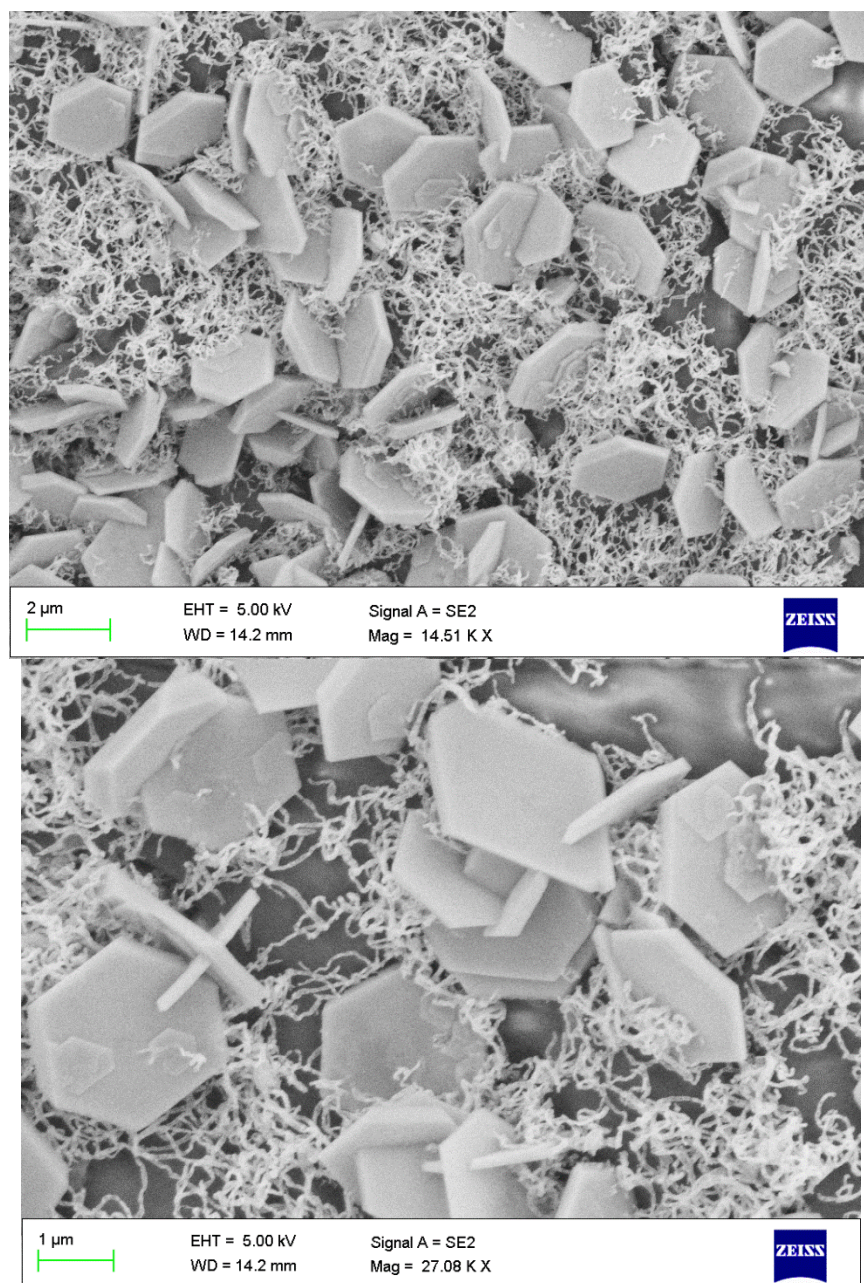


Figure 15: SEM image of Silver nanowire after conducting Ferrocyanide test

SEM images clearly showed that the platinum particles were leached out from the Silver nanowire. This leaching out of the Platinum particles can be avoided by using proper Capping agents and carrying out the process at lower scan rate potential.

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