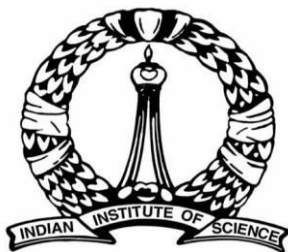


DEPOSITION OF PURE PALLADIUM BASED STRUCTURES FOR HYDROGEN SENSING APPLICATIONS

*A project report submitted
in completion of Summer
Internship-2018 by
Reema Daswani*



Department of Chemical Engineering

Indian Institute of Science

Bengaluru 560012

July 2018

ACKNOWLEDGEMENT

Any project cannot be completed successfully without the support and guidance of learned people. I am very grateful to **Dr. S.Venugopal** for providing me the opportunity to do a small project under his supervision. I also thank him for always clearing my doubts with patience and inspiring me in many ways. I would also extend my sincere thanks to my mentor, Abhishek Ranade for always being supportive and guiding me through each step.

Abstract- Hydrogen is considered as the sustainable fuel of the future as it has highest calorific value, abundantly available and a clean energy source. However, hydrogen concentrations higher than 4% v/v in air are highly flammable .Hence it is crucial to fabricate low-cost and fast-response hydrogen sensors to detect any leakage while transporting, handling and storage. Also it is required that these sensors are flexible so that they can be used to detect hydrogen leaks around pipelines. The common problem with the commercial sensors available at present is that they operate at high temperature (around 300°C) .Palladium based hydrogen sensors have become promising devices to monitor hydrogen concentrations due to high catalytic activity towards hydrogen. The basic working principle behind these sensors is that when hydrogen is adsorbed on palladium, Palladium hydride is formed leading to changes in electrical, optical and mechanical properties. These changes are then translated into an electrical signal by means of a transducer which can be used to monitor hydrogen concentration. Reducing the dimension of the palladium structures to Nano scale increases the specific surface area of Palladium leading to an increase in the rate of adsorption of hydrogen. This suggests that it is possible to fabricate fast response hydrogen sensors which can operate at room temperature by reducing the dimension of the palladium structures.

In this project our aim is to create conductive palladium nanostructures on flexible substrate using low cost methods. Various methods including print-expose-develop and electroless deposition were tried for fabricating conductive palladium structures on drawing paper and the testing was done using a set up to detect hydrogen in flow through conditions built in accordance with the guidelines specified by **ISO 26142**.

INTRODUCTION

With an ever increasing energy demands and continuous depletion of non-renewable energy reserve, there is an ongoing research for sustainable energy fuel which will serve as an alternative to the fossil fuels. Hydrogen is considered as one of the best alternatives as it has very high calorific value and is abundantly available. Whether hydrogen is burned to produce heat or reacted with air in a fuel cell, the only byproduct is water vapor that does not pollute the environment unlike fossil fuels.

But the only major concerns with using hydrogen as a fuel that it is highly flammable gas which is explosive above 4% v/v content in air. Hydrogen, unlike gasoline is odourless and it is a very small molecule with low viscosity which makes it prone to leakages. Hence it is not possible to detect hydrogen with odour. Thus, hydrogen sensors with fast response have a major role to play in the envisioned hydrogen economy.

Presently, hydrogen sensing is necessary in areas like ammonia and methanol production, the hydration of hydrocarbons, the desulphurization of petroleum products and the production of rocket fuels. Palladium's high affinity towards hydrogen makes it an apt choice for sensing electrode material. The selectivity of Platinum towards hydrogen is comparable to Palladium but

its sensitivity is higher compared to the latter. Pure palladium structures are prone to mechanical damage on exposure to hydrogen which limits the longevity of the sensor. Also, palladium sensors have to be protected against carbon monoxide, sulphur dioxide and hydrogen sulphide as they act as poison for hydrogen absorption. Hence Palladium based alloys are gaining popularity for sensing and other applications. Hydrogen atoms randomly occupy the octahedral interstices in the Pd-metal fcc-lattice. The surface sites of palladium then proceed to fill with hydrogen, leading to the formation of PdH_x and the increased resistivity of individual Pd nanoparticle. The Pd volume expansion, due to hydrogen adsorption, then initiates a drop in resistance. Thus variation in resistance is observed in the transient response during hydrogen adsorption on Pd.

Upon exposure of Pd to H₂ the gas molecules get adsorbed on the surface of Pd and thereafter get dissociated into individual atoms. The hydrogen atoms continue moving by diffusion through high diffusivity ways like grain boundaries, dislocations or even by vacancy exchange mechanism and ultimately occupy an octahedral interstitial site in the Pd lattice

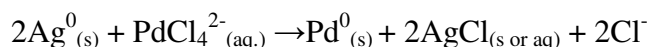
The Pd nanostructures exhibit high sensitivity and fast response times but it gets saturated very fast at high hydrogen concentration which hinders its applications. One way to resolve this issue is to use Pd alloys which enhance the stability of the fabricated sensors.

ISRO uses Liquid hydrogen as a fuel in space shuttle launches. Hence during storage, transportation and handling, there are chances of leakage through the pipe hence it is required that there should be flexible and effective hydrogen sensors. The essential components of an effective hydrogen sensor are high sensitivity, hydrogen selectivity, low response times (less than 1 second), low cost of fabrication, low power consumption, reliability and better lifetime.

BACKGROUND

Pd coated Ag nanowires were used for hydrogen sensing application. To form silver nanowires on paper, print-expose-develop technique was used. This involves printing alternate layers of AgNO₃ and 0.1M KBr/KI on paper using inkjet printer to print AgBr on paper, which is otherwise sparingly soluble in water. Once the photosensitive compound AgBr is printed on paper, it is exposed to halogen lamp for 20min which reduces it to active silver clusters. After this the sample is immersed in D-76 developer for 15 min which induces Ag⁺ ion mobility. Pd coating was done using galvanization in which the sample containing silver nanowires was immersed in 0.00133 M PdCl₂ solution for 15 minutes.

Galvanic exchange process reaction between Ag and Pd--



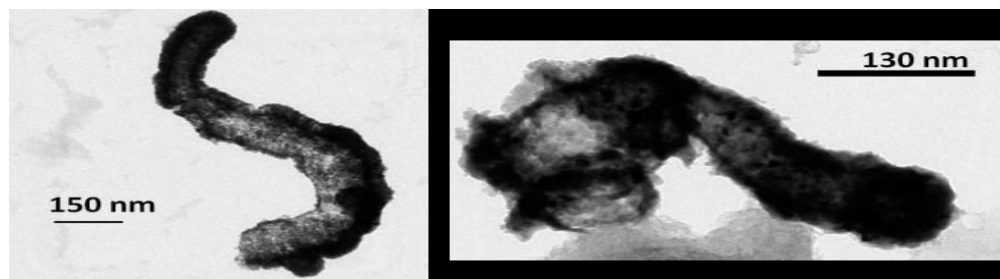


Figure 1: Ag nanowire with non-uniform deposition as seen in TEM imaging

Pd lumps were formed as observed under a Transmission electron microscopy imaging. Ag content decreased which suggested that it was replaced by Palladium. But the hydrogen sensing response was not reproducible as the coating was not uniform. Hence pure Palladium structures were fabricated to serve as reference for the hydrogen sensing applications.

METHODS TO CREATE PURE PALLADIUM STRUCTURES

1) Seed Growth Method-

14mg PdCl_2 was dissolved with 33.6mg citric acid in 20ml DI water for 2 hours. The solution was drop casted on a paper substrate. After that equal volume of 0.1 M NaBH_4 was drop casted for reducing Pd^{+2} ions to Pd. The paper substrate was subsequently rinsed and dried. Iridescence was observed but no conductivity was found. SEM analysis showed Palladium seed formation. For growth of the seeds, the substrate was kept immersed in Palladium nanoparticle solution (formed by mixing 8ml of 4mM solution PdCl_2 solution with 8mg coffee). Subsequently, the substrate was rinsed and dried but still no conductivity was observed as expected by us which shows the final palladium coating on paper was not sufficient so as to form a conducting path.

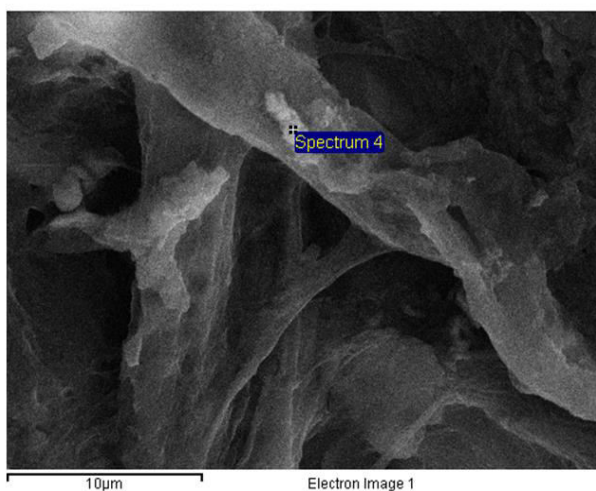


Figure 2: Seed like formation seen under SEM imaging of paper drop casted with PdCl_2 followed by NaBH_4

Element	Weight%	Atomic%
C K	48.32	60.33
O K	39.73	37.24
Al K	0.95	0.53
Si K	1.04	0.55
Cl K	0.30	0.13
Ca K	0.91	0.34
Pd L	2.20	0.31
Ag L	1.10	0.15
Au M	5.45	0.41
Totals	100.00	

Elemental analysis using Energy-dispersive X-ray spectroscopy

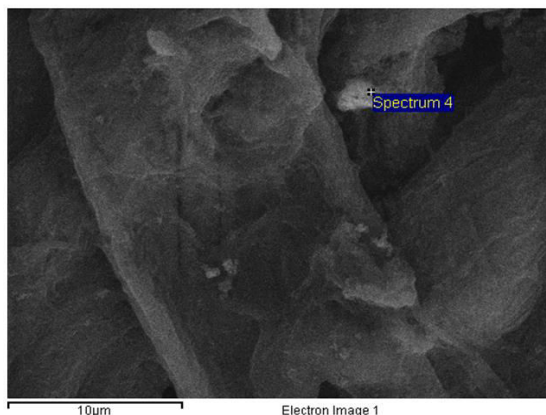


Figure 3:SEM image of sample after immersing the paper with -seed sample in Pd particle solution stabilised by coffee molecules.

Element	Weight%	Atomic%
C K	27.79	58.78
O K	18.34	29.13
Pd L	44.13	10.54
I L	4.21	0.84
Au M	5.53	0.71
Totals	100.00	

Elemental analysis using Energy-dispersive X-ray spectroscopy shows considerable increase of palladium content in the seed.

2) Print-Expose-Develop

Analogous to the print-expose-development for deposition of silver ,the same technique was tried for palladium printing. Here ammonium tetrachloropalladate solution is prepared and a sensitizer solution is added to it to make it photosensitive. After 0.2M EDTA solution is used for development.

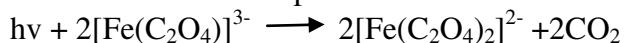
Experimental Procedure-

160 microlitre of ammonium tetrachloropalladate solution is prepared by adding 12 mg of ammonium chloride, along with 20 mg of PdCl_2 and it is kept for dissolution for 1 hour. Ammonium trioxalatoferrate (1.4M) is added which serves as a sensitizer solution .After it the above solution is drop casted on paper samples and kept for drying. Subsequently it is exposed to UV light. The samples are exposed for different duration to study the effect of different exposure time. After exposure, EDTA is used for development in the process.

Mechanism-

The ferric oxalate complex undergoes a photochemically-induced redox reaction, yielding carbon dioxide and an oxalate complex of iron(II).

The reaction can be represented as-



The above reaction is spontaneous but involves kinetic barrier which can be overcome only when the complex is photoexcited by absorption of ultra-violet light in the vicinity of its ligand-to-metal charge transfer band at maximum wavelength 260nm.The

iron(II)oxalate-complex thus formed is quite a powerful reducing agent which reduces the ammonium tetrachloropalladate salt to Pd. The molar ratio of Pd :Fe is kept 1:2.



Development is done by washing with EDTA as it is very effective in removing excess unreacted iron (III) from paper.

Observation-

The samples were yellowish-brown prior to exposure to UV lamp. After exposure to UV radiation the colour becomes black. The conductivity was measured with a multimeter. The resistance values for the samples exposed for 1min, 5min and 15min were 217 kilo ohm, 222kilo ohm and 0.466 Mega ohm but the conductivity was lost after immersing it in developer solution for 15min. And also the same experiment was repeated with for sensitizer solution palladium complex separately. The exposure time was kept 15 min for both. The sample with the sensitizer solution showed resistance value of 0.6 Mega ohm which was lost once it was dipped in EDTA developer.

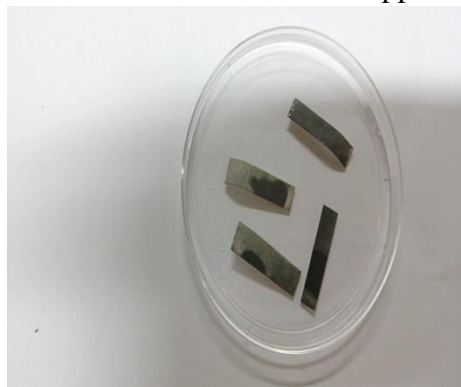
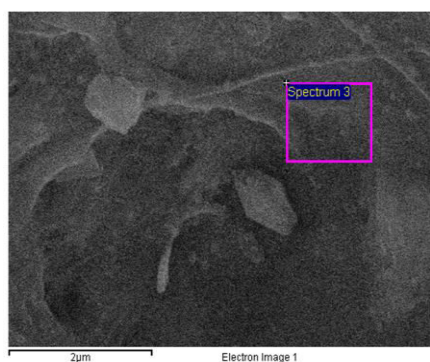


Figure 4: The sample containing ammonium tetrachloropalladate and sensitizer turn black upon exposure to UV light



Element	Weight%	Atomic%
C K	0.00	0.00
O K	59.33	85.34
Ca K	16.37	9.40
Pd L	24.31	5.26
Totals	100.00	

15min

Figure5: SEM and EDS analysis of sample kept for 1 min exposure in UV light

Element	Weight%	Atomic%
O K	61.63	92.25
Cl K	0.00	0.00
Pd L	29.78	6.70
Au M	8.59	1.04
Totals	100.00	

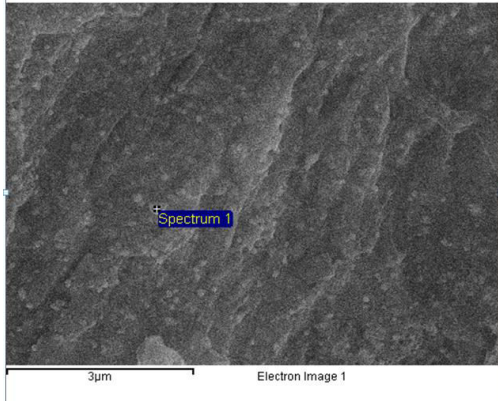


Figure 6:SEM and EDS analysis of sample kept for 15 min exposure in UV light showing particulate structures on cellulose fibres

Inference-

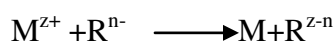
The conductivity observed is due to iron only and not palladium as expected by us. Hence, this method cannot be used to create conductive palladium film on paper as desired for sensing applications.

3) **Electroless deposition** is a process that has been used in practice for centuries. It can be defined as a deposition of solid phase of continuous coating or powders of metals, alloys, or compounds from aqueous or nonaqueous solutions or melts without an external current source. The advantage of this process is that it is cost effective as it does not require any external current source and also nonconductive substrate can be used with uniform coating as well. Few things to consider when autocatalytic deposition takes place is

- 1) The metallic ion reduction can take place in the bulk solution or only at the catalytically active surfaces. If deposition is being carried out at the solid surfaces, the surfaces must be activated properly.
- 2) The concentration of the reducing agent must be properly chosen to avoid reduction in the bulk solution followed by precipitation of metallic powders.
- 3) All the parameters influencing the rate of redox reaction (e.g. temperature, pressure, concentrations of additives, and chelating agent) have to be very carefully controlled to achieve the desirable thickness and properties of the deposit.

4) The growth of the film is influenced by the catalytic activity of the surface on which a metal is deposited.

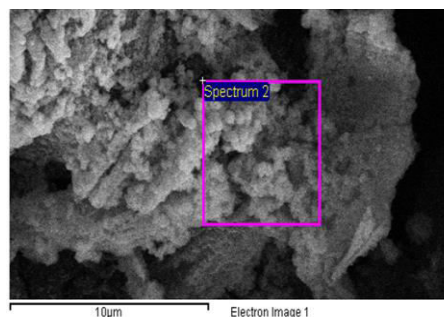
The electroless deposition of a metal M , using a reducing agent R^{n-} , can be described with the following generic reaction:



The deposition at the surface occurs as a continuous film with a uniform surface morphology. The increase in concentration of the reducing agent or temperature, the deposition of powders occurs, a phenomenon which is usually described as “bath instability.”



Figure 7:Black deposit with lustre formed due to palladium deposition after electroless plating on paper



Element	Weight%	Atomic%
O K	21.04	61.77
Si K	4.03	6.73
Cl K	0.76	1.00
Pd L	47.75	21.08
Sn L	19.80	7.83
Au M	6.63	1.58
Totals	100.00	

Figure 8: SEM Imaging and EDS analysis of paper after electroless deposition. Nano filament like structures are seen on cellulose fibres

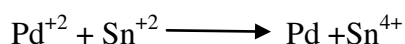
Electroless deposition was tried to form a thin film of paper on Palladium substrate. It basically involves three steps-sensitization, activation and immersion in a suitable bath. Sensitization with acidic $SnCl_2$ is required to create active tin sites on paper. After that activation is done to replace the active tin sites with the Pd. Sensitization prior to activation is necessary as Pd doesn't react directly with a substrate due to its inert nature. After that, it was immersed in a hydrazine bath for a day. The conductivity of the substrate was found to be 0.6-1 kilo ohms. The exact method is listed below

1) Sensitization-20 ml solution was prepared which comprised of 20g/l of SnCl_2 along with 10ml/l of HCl solution. The solution was stirred continuously at 25C. After this the substrate was rinsed with DI water

2) Activation /Alternate activation-The substrate was activated for 15 min by immersing it in 20 ml solution of 16 mg PdCl_2 and 0.576g of SDS. SDS is a reducing and stabilizing agent for the nanoparticles. Here Pd nanoparticles are formed which replace the active Sn sites formed due to sensitization. An alternate bath comprising of Pd nanoparticles was also used for another to study the effect of nanoparticle size on conductivity. In this 2ml of 4 mM solution of PdCl_2 was prepared and 32mg coffee powder was added which also acts like a reducing and stabilizing agent. Both the activation methods were done at 50C. After this step, the solution was rinsed with DI water and kept for drying.

3) Immersion in reducing bath-The substrate was kept in a 10 ml reducing hydrazine bath for a day after the active Pd sites were created on paper. First 40.7 mg PdCl_2 was dissolved in 60 microlitre of HCl (38%) and 10ml DI water. On complete dissolution, 3ml of ammonia solution was added for pH adjustment followed by EDTA, which acts as a chelating agent. 2.5mg of hydrazine was added to reduce the Pd^{+2} ions in solutions. The activated substrate was then immersed in it and heated to 60 degree Celsius.

The mechanism involves deposition of Sn^{+2} particles on paper in the sensitization step. In the activation step following reaction takes place-



Tin not only acts as the reducing agent for Pd ions, it is also claimed to stabilize the small Pd nuclei once they form via strong Sn^{+4} adsorption. However excess ionic tin on the surface of the particles is detrimental to the plating process. After deposition of the catalyst particles on the surface, the tin shell is removed in the bath step. In the bath step, the substrate oxidized the reducing agent i.e. hydrazine here due to which deposition occurs at the substrate here. If the concentration of the reducing agent is further increased deposition occurs in the solution itself.

The average Pd content was found around 50% by weight in the EDS analysis. The morphology suggested that there was a thin film coating of Pd structures on cellulose fibres. The response time (including diffusion) was found to be around 40s and actual response time was around 10-15s.

SET UP FOR TESTING-

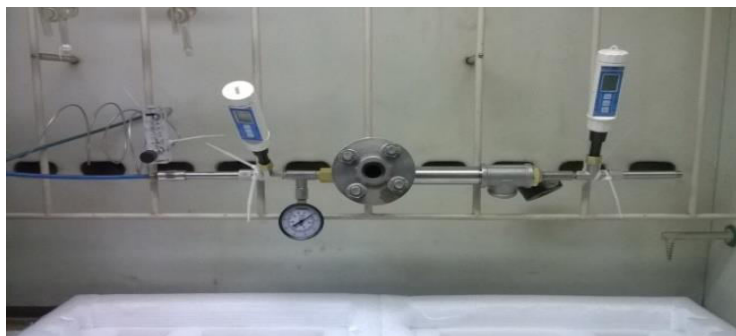


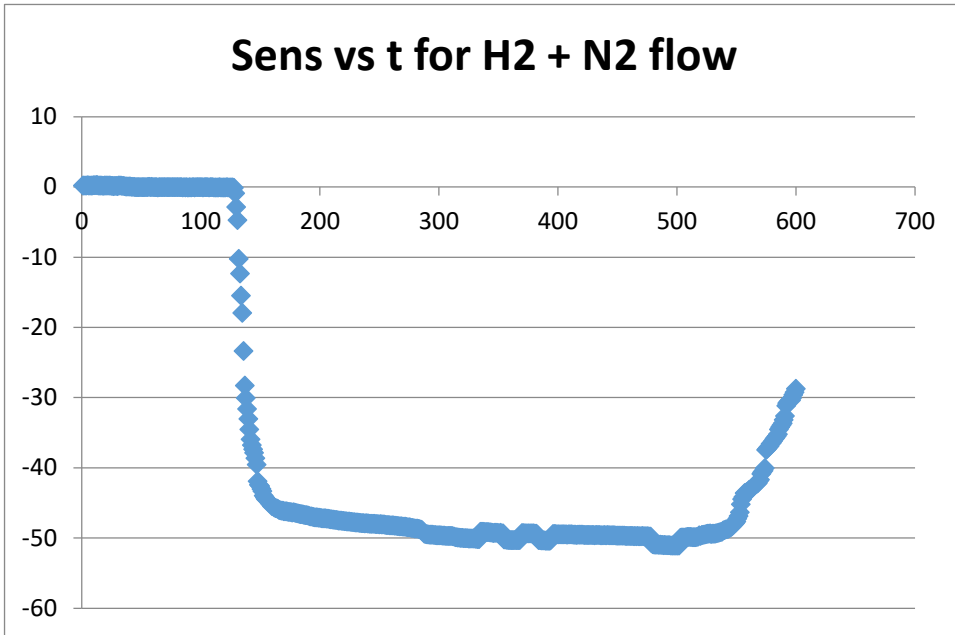
Figure 9: Flow through setup made for hydrogen sensor testing as per ISO 26142 guidelines

In this set up, the testing is done for hydrogen in a flowing case. First a hydrogen generator is used which produces hydrogen gas using KOH as input.

H₂ gas is passed along with N₂ gas. Rotameter is used to control the flow rate of both the streams. The flow rate of H₂ is kept at 300ml/min and that of N₂ is kept at 2.5l/min so as to keep 11% volume ratio of hydrogen to Nitrogen. Both the streams pass in a single tube through connector. The tube has connected pressure gauge and temperature and humidity meters to measure the conditions of flow. After flowing through a certain distance hydrogen gas encounters the sensor. The sensor is encompassed with circular disc like structure on both sides. This structure ensures that there is no leakage of gas. Both the sides of the sensor is connected to nanovoltmeter and nanoammeter to monitor resistance changes. The gas is vent out to the atmosphere through the other end of the tube.

HYDROGEN SENSING RESPONSE

First to measure the base resistance of the sensor only nitrogen is passed for 5 min duration until the resistance value is stabilized. Subsequently, the hydrogen gas testing is done for 10 min duration. The resistance decreases which can be attributed to volume expansion of Palladium lattice due to hydrogen absorption. After stopping hydrogen flow, the resistance value is restored to its original value due to desorption. Here sensitivity is defined as per cent change in the resistance divided by the base resistance (measured when only nitrogen is flowing). The response time is defined as the time taken to achieve 90% of the steady state value. The sample for which electroless deposition is done for 28 hours showed a response time of 40 seconds (including the time for the gas to flow to the sensor). Hence the actual response time of sensing is lower than this.



CONCLUSION

Electroless deposition is an effective and low cost technique for depositing a conductive Palladium thin film on paper. Pure Palladium is prone to cracking under stress. Hence the Palladium loading has to be kept optimal. Palladium based alloys are an effective solution for this problem. The response time for hydrogen sensing of pure palladium structures is less than that of bimetallic Ag-Pd structures which is expected due to high sensitivity of Palladium towards hydrogen. The response time for pure Palladium film on paper deposited by electroless deposition is 40 seconds which is quite low. But the desired response time is less than 1 second. Therefore, we can say that for effective hydrogen sensing applications Palladium based alloys with different morphologies have to be explored.

REFERENCES

- 1) Citation: CUI, X. ... et al, 2011. The evolution of Pd/Sn catalytic surfaces in electroless copper deposition. Journal of the Electrochemical Society, 158 (3), pp.D172-D177.
- 2) S.S. Djokić (ed.), Electrodeposition: Theory and Practice, Modern Aspects of Electrochemistry 48, DOI 10.1007/978-1-4419-5589-0 6, c Springer Science+Business Media, LLC 2010
- 3) An Investigation of Platinum and Palladium Printing Mike Ware [First published in The Journal of Photographic Science 34 (5/6), 165-177 (1986).]
- 4) Electroless plating of ultrathin palladium films: self-initiated deposition and application in microreactor fabrication cite this article: Falk Muench et al 2015 Mater. Res. Express 2 105010
- 5) METHOD OF ACTIVATING NON-CONDUCTIVE SUBSTRATE FOR USE IN ELECTROLESS DEPOSITION Pub. No.: US 2002/0197404 A1
- 6) Sn-Ag 2step activation process for electroless copper plating .Hong-Kee Lee, Jin-Young Hur, Ho-Nyun Lee, Chang-Myeon Lee Korea Institute of Industrial Technology 7-47, Songdo Dong, Incheon Korea