HYDROGEN GAS SENSOR ON PLASTIC SUBSTRATES

Abhishek C. Ranade, Kalyan Nandakumar and Venugopal Santhanam

Abstract—**Nanostructured conductive thin films comprising of palladium coated silver have been fabricated on plastic substrates using a simple office inkjet printer and room temperature chemical processing. The use of instant coffee powder to enable uniform deposition of palladium on top of silver nanowires was the critical step. We also have set-up hydrogen testing apparatus, as per ISO standards, for dynamic as well as response time measurements. The results indicate that hydrogen absorption induced nano-gap closing leading to higher conductivity is the mechanism of detection. Preliminary tests indicate that silver nanowire samples placed in palladium toning solutions for one week have a similar Pd/Ag content as the samples toned for one day. But, the response of the one-week toned sample (38 s) is an order of magnitude faster.**

I. INTRODUCTION

Hydrogen is a fuel of the modern era that is efficient, green, sustainable and abundantly available. At the same time, it is also highly flammable and highly prone to leakage. Hydrogen pipelines at LPSC span a length of few hundred metres and represent a significant safety concern. Distributed gas leak detectors based on chemochromic (Colour-changing) 'tapes', which rely on nanostructured metal oxides, have been recently developed to monitor pipelines in NASA [1,2]. Herein, we propose to build on the results of our earlier investigation on silver-palladium alloy nanostructures (*ISTC-286*) and develop distributed gas leak detectors consisting of electrical transducers on plastic substrates for hydrogen leak detection.

Palladium-based sensors have been the most popular choice for detecting hydrogen [3]. Palladium forms palladium hydride (Pd-H$_x$) when exposed to a hydrogen atmosphere. However, palladium hydride exhibits hysteretic behaviour that is detrimental to sensor performance. Palladium silver alloy nanostructures, with a palladium rich shell, can avoid such hysteretic behaviour due to confinement induced restriction on structural expansion [4,5]. Our earlier attempts at fabricating palladium rich shell by Galvanic displacement of silver led to non-uniform deposition of palladium (Fig. 1). So, we decided to systematically investigate methods for fabricating a uniform shell of palladium on silver nanostructures with different morphologies. During our work, we also realised the need to develop sensor testing facility as per ISO standards, both for facilitating comparison of performance characteristics with other sensors and for avoiding drift and noise in the measurements made with our previous setup. In this report, we discuss the results of our investigations along these two aspects.

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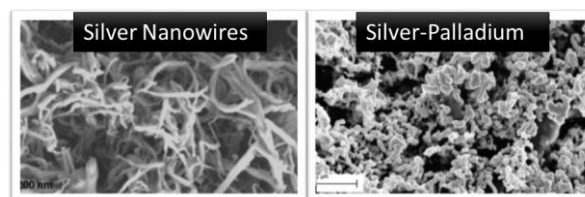
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Fig. 1. Morphology of silver nanostructures obtained by Print-Expose-Develop process, and silver-palladium alloy nanostructures obtained after Galvanic displacement.

II. FABRICATION PROCESS

Preliminary investigations were performed to optimise conditions for the formation of a uniform palladium coating. For these experiments, silver nanowires were formed *in situ* on paper by depositing a silver bromide film using an office inkjet printer, followed by exposure to light and development in a commercial photographic developer solution. The resultant silver nanowire networks on paper were transformed into palladium-silver alloy nanostructures by using a standard palladium 'toner' recipe comprising of 3.98 mM of PdCl$_2$ and 80 mM of citric acid monohydrate. However, the results indicated that Galvanic displacement was occurring to a significant extent, based on the appearance of silver flakes floating on top of the solution. To suppress this undesired effect, we added BRU-instant coffee powder, about 159.1 mg to 10 mL of the above toner recipe. Coffee contains caffeine/polyphenols that can form complexes with metal ions in solution and stabilise them. To activate the surface for toning, the sample was first immersed in a 0.156 M solution of citric acid monohydrate for I h (paper-based samples) or 8 h (OHP sheets), before dipping in the coffee-added toning solution. This activation step was found necessary as there was no palladium plating without such activation.

III. RESULTS

Microscopic and spectroscopic characterisation of the nanostructures on paper after palladium toning confirmed the presence of palladium and the formation of a uniform coating in the presence of coffee. Fig.2 shows representative FESEM images that highlight the effect of adding coffee powder on the morphology of palladium-silver nanostructures formed. In the absence of coffee powder. The resultant nanostructures resemble those formed using Galvanic displacement method; while with the addition of coffee powder the nanostructures retain their original wire-like morphology. EDX analysis of the domains marked by the rectangular frame in figure 2 confirm the presence of palladium, in a ratio of about 1:4 (atom%) with silver. Interestingly, Cl signals corresponding to PdCl$_2$ was also detected in the case of the sample prepared without adding coffee. However, Cl signal was completely absent in the case of the sample prepared with the addition of coffee. These results confirm the successful formation

of a uniform coating of metallic palladium on silver nanowires, in the sample prepared with added coffee powder, if any. Modelling the toning process as a uniform coating of palladium on a 70 nm diameter silver nanowire (nominal nanowire size), and assuming an atomic ratio of 1:4, as measured by EDX analysis, the palladium coating is expected to be about 8 nm thick.
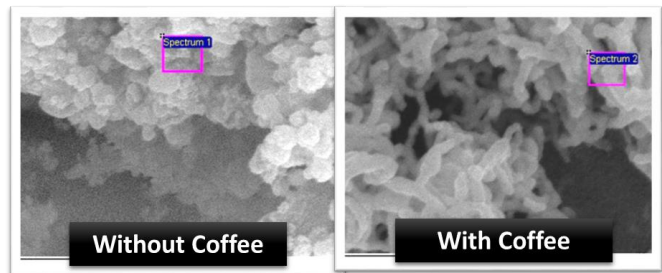

Fig. 2. Morphology of palladium coated silver nanostructures obtained by utilising a palladium toning solution with and without added coffee powder.

Since paper was considered as a flammable hazard for use in ISRO facilities, alternative substrates were explored. In this report, consideration is given to commercially available overhead transparencies. Overhead transparency sheets (PET) were selected as the substrate since they are flexible and inexpensive. However, unlike paper, they cannot retain aqueous-based printing inks, in that they are hydrophobic. After various attempts, we discovered that simply roughening the OHP sheet using P220 sandpaper rendered the OHP sheets hydrophobic. Optical profilometry indicated that indeed the roughness had increased from an average value of 0.01 μm to 4.42 μm after roughening with sandpaper. This was enough to not only make the OHP surface wettable, but also provide adhesion to the printed silver pattern so that it did not wash away during the development step. This procedure was also applicable to other plastic substrates such as polyimide tapes.

Based on the success of adding coffee powder, the following samples were prepared (Table 1) and their hydrogen response characterised. Previously, the sensing performance of Pd-Ag nanostructure were carried out in a testing set-up available at CeNSE, IISc. As the setup was designed for rigid substrates, the gas flow was directly aimed at the substrate. However, this is problematic in the case of flexible substrates such as paper or thin plastic sheets and led to excessive electrical drift and noise, which is attributed to the fluttering of the flexible substrate and subsequent electrical contact changes. To avoid such issues, we have set-up a dedicated hydrogen gas detection apparatus, as per ISO standards [5]. Figures 3 and 4 show schematics of the test apparatus recommended by ISO, as well as the realisation of such a set-up in our lab for dynamic flow-through experiments and static response time measurements. These set-ups were used to characterise the hydrogen leak detection capability of our samples and compare them with the other available distributed gas leak sensors on the market.

Table 1: Samples prepared for testing in diffusion chamber and flow through setups

| Sample label	Pd /Ag ratio, (EDX)	'Coffee-added'	Substrate	Base resistance R_0 (Ω)	Palladium deposition time (h)	PdCl$_2$ concentration used for toning (mM)	Hydrogen Dosage (H$_2$ conc, % /time, s)
a	0	-	Paper	17	-	-	10.7 / 360
b	0.08	Yes	Paper	29	1	4	100 / 540
c	0.32	No	Paper	248	1/2	4	10.7 / 360
d	0.51	Yes	Paper	717	24	4	10.7 / 360
e	0	-	OHP	60	-	-	10.7 / 360
f	1.06	Yes	OHP	205	24	4	10.7 / 360
g*	1.06	Yes	OHP	205	24	4	10.7 / 120
h	1	Yes	OHP	1054	168	8	10.7 / 120
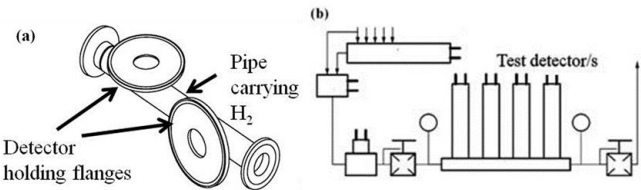
Fig. 3. Top-Schematic view of ISO recommended dynamic flow-through setup. Bottom-Flow-through setup for hydrogen sensor testing as per ISO 26142 guidelines.
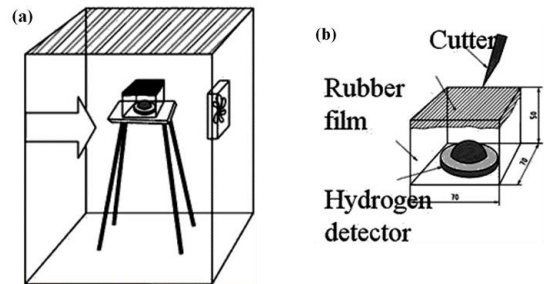

Fig. 4. Top-Schematic view of ISO recommended static response time setup. Bottom-Realisation of static-response time setup for hydrogen sensor testing as per ISO 26142 guidelines.

III.a Flow-through setup

The measurement of changes in resistance of the test samples subjected to various gas phase environments in the flow-through test set-up are summarised as plots of sensitivity ($\Delta R/R0$) vs time (Figure 5). In these plots, the red coloured portion of the curves represents the duration during which hydrogen flow was added onto the base flow of nitrogen to achieve the desired concentration.
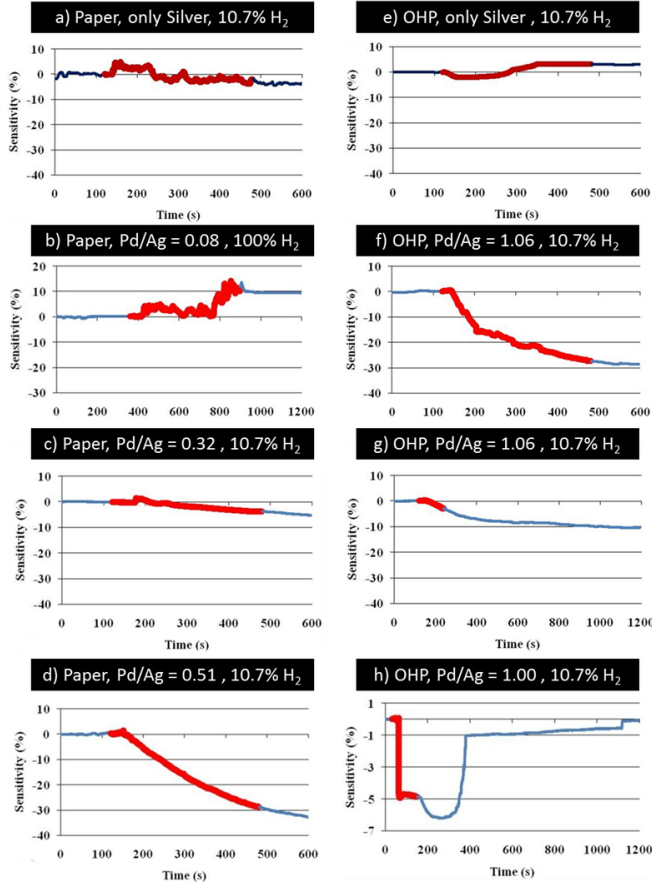

Fig. 5. Measured responses of the various samples tested using the flow-through test setup. The red coloured portion of the curves represents the duration during which hydrogen flow was added onto the base flow of nitrogen. The key characteristics of the samples are summarised above the individual response curves.

The crucial observations based on the results of the flow through tests are:

(i) Role of Palladium

The need for palladium to detect hydrogen is evident from figure 5. With palladium, the sensitivity change upon exposure to hydrogen is more prominent, monotonic and well above the noise level (0.24%), while the sample without palladium shows random fluctuations (RMS value ~ 2.32%).

(ii) Effect of palladium content

The Pd/Ag ratio as measured by EDS is an indicator of the palladium content of the detector. Pd/Ag ratio ≥ 0.32 leads to detectable signal upon hydrogen exposure. For most of the samples, the resistance (and sensitivity) drops upon exposure to hydrogen. The decrease in resistance indicates that the effect of expansion on electrical conductivity is more significant than the formation of palladium hydride. For the sample with Pd/Ag ratio of 0.08, the sensitivity fluctuated initially for about 400 s and after that showed a clear increasing trend. We conjecture that there is not sufficient palladium in the network to affect the percolation pathway by expansion, and so the response is slow, and resistance increases after most of the palladium is converted to palladium hydride. Interestingly, even after switching off the hydrogen supply, the response continues with the same decreasing trend till saturation is reached. We suppose that the plastic sealant bags act as an additional reservoir (capacitance) that limits the ability to change gas composition suddenly. This aspect needs to be investigated more thoroughly in the future.

The samples regained their base value of resistance after being exposed to ambient conditions overnight. This suggests that hydrogen desorbtion from the nanostructured palladium coated films is reversible but slow.

(iii) Effect of hydrogen dosage

To investigate the effect of total dosage of hydrogen sample f was re-exposed (after the original resistance was regained – ca. 1 day) to the same hydrogen environment but for a shorter duration (denoted as sample g). The change in resistance was lower for lower dosage. This suggests that the extent of hydrogen absorption into palladium determines the magnitude of the response. The time taken for saturation of signal response is similar for both samples f and g.

(iv) Effect of toning time

A comparison of the response of samples f and h indicates that the duration of toning has a significant effect on the response rate of the palladium toned samples. The Pd/Ag ratio measured using EDX was similar for the samples toned for 1 day and 1 week, while the base resistance increased from 205 Ω to 1 kΩ. Although the Pd/Ag ratios are representative of the sample, they may need to be verified independently using a bulk technique. Presuming that the averaged EDX ratios are representative of the bulk composition, as the nanostructured films are less than a micron in thickness, the increase in base resistance with increased toning duration indicates that some of the silver in percolating paths are etched/displaced by palladium overlayer. This redistribution of the palladium at the junctions of the percolating network is the likely cause for the rapid response of sample h. This sample was also able to recover its base resistance value more rapidly. Such an architecture, wherein the palladium is present at the junction of percolating pathways is apt for rapid detection and provides an avenue for future detector-response optimization studies. Note: The palladium salt concentration was doubled, as a precaution, to account for any loss of activity during the one-week duration of the experiment.

III.b Static Response setup

To keep the test duration short and avoid interference due to unknown leaks, a hydrogen filling time of 3 min was chosen. After this the lid was displaced and the inner chamber opened up to an atmosphere of hydrogen (corresponding to 1.62 % H_2 with the sum of the outer and inner chamber volumes as the basis). The response of the sample toned for one week is much faster and more robust than the sample toned for one day (Figure 6). This again corroborates our hypothesis about the changes in morphology of the nanostructures being optimal for hydrogen detection. The leak

detection response time of sample h was estimated to be 332 s. In calculating the response times, the lowest value of sensitivity has been used as a saturation value to get its 90% value. The time taken to reach this value starting from the time when hydrogen was switched on is the response time.
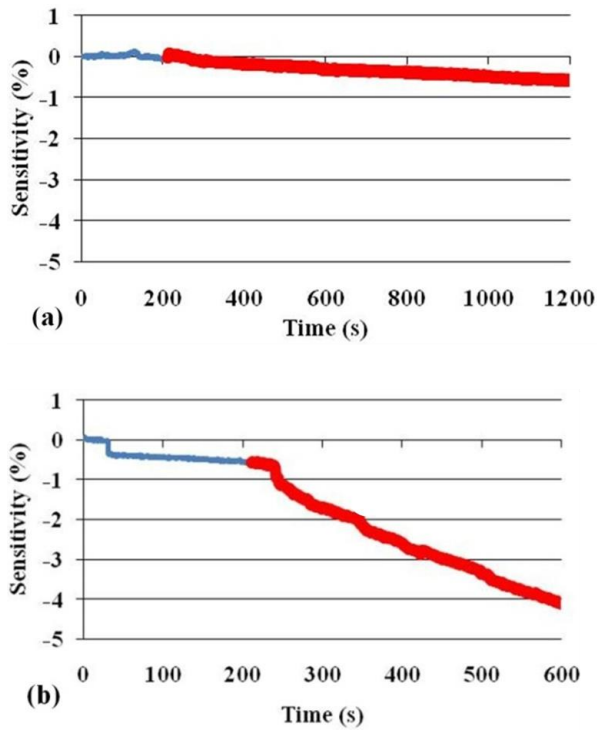

Fig. 6. Static leak test - response of samples upon sudden exposure to an atmosphere of 1.62% H_2 (a) sample d – Pd/Ag ratio of 0.51 on paper (b) sample h – Pd/Ag ratio of 1 on OHP.

Table 2 compares the values observed in this study with other reports in the literature using processes that can be scaled up for mass-production of palladium-based hydrogen detectors. The response time of the samples prepared in this preliminary study is comparable to that of samples published earlier. The colour changing leak detectors employed at NASA has a reported response time of lesser than 3 min at a hydrogen concentration of 1% [9].

Table 2: List of Pd based detecting elements/detectors and comparison of their response time with this work

Sr. No./ Year	Detecting element/ Substrate	Morphology	Fabrication method	Conditions	t_{90}	Refere-nces
1./(2009)	Pure Pd/ Si	Nanowires (400 nm)	Lithographic patterning	1% H_2 in N_2, RT	~250 s	[6]
2./(2008)	Pure Pd/Alumina	Nanowires	Electro deposition	1% H_2 in N_2, RT	~300 s	[6]
3./(2013)	Pd –Ag/PVC	Nanowires	Electro deposition	1% H_2 in air, RT	~150 s	[7]
4. /(2007)	Pure Pd/alumina	Thin film	E-beam evaporation	10% H_2 in N_2, RT	~2000 s	[8]
5.	Pd-Ag/OHP	Nanowires	Coffee toning, 1 week	10.7% H_2 in N_2, RT	38 s	This report
6.	Pd-Ag/OHP	Nanowires	Coffee toning, 1 week	1.62% H_2 in air, RT	332 s	This report

IV. SUMMARY

We have developed a process for coating palladium uniformly onto silver nanostructures. Test set-ups for hydrogen gas detection have been built as per ISO specifications. Based on the observations of the samples tested so far, the following conclusions can be arrived at:

1. Coffee powder is useful for suppressing the galvanic displacement of silver by palladium during the toning step.

2. Roughness is the key for good wettability as well as excellent adhesion of printed silver nano-wires on OHP substrates. Commonly-available sandpaper can be used to roughen plastic substrates and render them amenable to inkjet printing of aqueous salt solutions.

4. The salient points of the results of the preliminary experiments on hydrogen detector performance characterization are:

i. The detection mechanism is based on gap closure in samples with high palladium content, as the resistance of these samples drop after hydrogen exposure

ii. The sample toned for one week exhibited the fastest response and had a response time of 38 s upon being exposed to a gas flow having 10.7% H2, and 332 s upon exposure to a leakage of gas comprising of 1.62% hydrogen.

V. FUTURE WORK

Detector recovery is one of the most important aspects to be investigated. Till now, we have seen that in all the detector response curves, recovery was not seen within 20-30 minutes of conducting the test in the 24-hour coffee toned samples. However, recovery was seen within 10 min, when the toning time was increased to 1 week. A more systematic investigation of the effect of the silver /palladium loading of the nanostructures is required to identify compositions with faster response and recovery times suitable for real-world applications.

Different morphology of silver nanostructures can be studied, as it is expected that the nano-gap mechanism may be more prominent in silver nanoparticles instead of silver nanowire networks.

Incorporation of the hydrogen detector structures into Radio frequency identification (RFID) antenna structures can help retrieve signals from the detector remotely. This would be beneficial for avoiding risks to safety-personnel monitoring the hydrogen pipelines.

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