Research Proposal for STC

Project Title:

LEAK DETECTION TAPES FOR HYDROGEN PIPELINES

Submitted to:

ISRO – IISc Space Technology Cell
Indian Institute of Science
Bangalore 560 012

Investigator(s) from IISc**:** **Dr. VENUGOPAL SANTHANAM**

Co-investigator(s) from ISRO (LPSC): **Mr. S. INGERSOL**

Department of Chemical Engg
Indian Institute of Science
Bangalore 560 012

October 2018

APPLICATION FOR GRANT OF RESEARCH / DEVELOPMENT PROJECT

SECTION –A

1	Title of research/ development Proposal	**Leak Detection Tapes for Hydrogen Pipelines**
2	Name of the Principal Investigator Designation and Address	**Dr VENUGOPAL SANTHANAM** Assistant Professor, Department of chemical engineering Indian Institute of Science Bangalore Ph. (O) 91-80-2293 3113 E-mail: svgpal@iisc.ac.in Website: http://chemeng.iisc.ac.in/venu
	Name of the Co- Investigator (s) from IISc Designation and Address, Phone, Fax, Email, Mobile Numbers	NIL
	Name of the Co-Investigator(s) from ISRO Designation and Address, Phone, Fax, Email, Mobile Numbers	**Mr S. Ingersol** Group Director, Systems Reliability Spacecraft Propulsion and Sensors Liquid Propulsion Systems Centre, Bangalore-560008. Ph. 080-25037441 E-mail: singersol@lpscb.gov.in
3	Proposed duration of the research/development proposal	2 years
	Proposed date of commencement of the project	April 1, 2019
4	Amount of grant proposed for	**₨ 14,95,000**
5	Department of the institution where R & D project will be carried out Other department if any, which will co-operate in this study Details of financial support sought/obtained from other agencies	Dept. of Chemical Engineering, IISc
6	Specific Aim of the Project	Appendix B (Attached)
	Summary of Proposed research/facilities and objectives (brief statement about the proposed investigation, its conduct and the anticipated results in not more than 300 words)	Appendix B (Attached)
	Keywords Classification of the project	Appendix B (Attached)
7	Background and justification (Basis for the proposal with a brief review of state of the art in the subject, followed by an outline of the relevance and importance of the project, in particular, towards research/development/design related to ISRO programs	Appendix C (Attached)

8	Approach (details of the actual approach indicating how each of the objective listed in item 6 (a) will be achieved); deliverables, Task schedule and bar chart	Appendix C (Attached)
9	Previous work done in this or related fields Describe briefly any work done that is particularly pertinent to the proposal & list: (I) your personal publications in this & related areas	Appendix C (Attached)
10	Expected Contributions from ISRO collaborators	Appendix C (Attached)
11	Additional information	Appendix D (Attached)

I certify that a detailed technical report describing the research work/ procedure and its findings will be submitted before the closure of the project.

Date: 30/10/2018 Signature of the Principal Investigator

APPENDIX – A

Project Title:

LEAK DETECTION TAPES FOR HYDROGEN PIPELINES

Amount of Grant Proposed: **Rs 14 95 000**

Grants (in Rs)	I Year	II Year	Total
(a) Salary # @ Rs 24000 PM for 1st year @ Rs 26000 PM for 2nd year	2 88 000	3 12 000	6 00 000
(b) Equipment⊗	NIL	NIL	NIL
(c) Working Expenses*	3 50 000	3 50 000	7 00 000
Sub-Total	6 38 000	6 62 000	13 00 000
(d) IISc Overheads @ 15%	95 700	99 300	1 95 000
Total	7 33 700	7 61 300	14 95 000
		Grand Total	14 95 000

#Salary for number (specify no. of position) of project associates/project assistants/others

1. Project Assistant: (One) @ Rs 24 000 PM in 1st year and @ Rs 26 000 PM in 2nd year.

***Working Expenses** include Stationary, Consumables and components, chemicals, minor fabrication costs (whichever is needed), TA/DA, etc. (Give a list of important consumable/components with approximate cost).

List of important consumables:

High purity chemicals: - Palladium salts, silver salts, gas cylinders and consumables for hydrogen generator and test set-up (1,50,000), Microscopic and Spectroscopic Characterization Equipment usage charges (2,00,000).

APPENDIX – B

Project Title:

LEAK DETECTION TAPES FOR HYDROGEN PIPELINES

1. SPECIFIC AIM/ OBJECTIVE OF THE PROJECT:

1) To design and optimise the morphology of silver@palladium nanostructures on polyimide tapes for leak detection along hydrogen carrying pipelines
2) To design and incorporate a printed heating element for enhancing sensor recovery and hydrogen sensing performance

2. SUMMARY OF PROPOSED RESEARCH:

We propose to build on the results of our ongoing investigation on silver-palladium alloy nanostructures for hydrogen sensing (ISTC/MCE/VS/385), wherein we developed a robust process, using coffee powder to control palladium coating on inkjet-printed conductive silver nanowire films. These films were formed either on paper or flexible plastic substrates. Structural and spectroscopic characterizations demonstrated the successful formation of a palladium layer on top of the silver nanowires. Meanwhile, we have fabricated a hydrogen sensor testing setup suitable for flexible substrates and conforming to ISO specifications. The ongoing tests indicate that the closing of percolation pathways due to the expansion of the palladium matrix caused by hydrogen absorption, and a concomitant decrease in electrical resistance was the mechanism of sensing. In this proposed project, we plan to optimize a palladium "toning" step further to coat these nanostructures onto polyimide tapes that can be wrapped around pipelines for leak detection. We also propose to incorporate a heating element to enhance hydrogen desorption and hence sensor recovery timescales. The development of flexible hydrogen leak detectors using a low-cost fabrication process will pave the way for improved safety while handling hydrogen, an issue of growing importance to ISRO as well as the developing fuel cell based 'hydrogen economy'.

Keywords:

Hydrogen sensor, Metallic nanostructures, Inkjet printing, Leak detection

APPENDIX – C

Project Title: Leak Detection Tapes for Hydrogen Pipelines

Background and justification:

Hydrogen (H_2) is emerging as a new source of energy to address the need for finding alternative renewable sources of energy and the concerns of global warming [1]. There are various advantages of using hydrogen as the source of energy as it undergoes "clean" combustion, and as it is feasible to be generated and recycled in a renewable fashion using water and solar energy. However, it is highly flammable with its lower explosive limit being 4% v/v in air [2]. Moreover, it is a colourless, odourless and tasteless gas, which means human senses cannot detect it. It is also the lightest element in the universe, which means its leakage risk is high. It might seem that adding some odorant (e.g. ethyl mercaptan used in cooking gas) will solve this problem. However, odorants are not suitable in case of smelling hydrogen leaks as they are not light enough to 'travel with' hydrogen or to disperse at the same dispersion rate. Also, in case of remote pipelines carrying hydrogen adding odorant will not make any sense. Hence it is imperative to have a system for fast and reliable detection of hydrogen gas in all the areas dealing with hydrogen.

The history of detecting and concentration monitoring of hydrogen dates back over 100 years, at filling stations for airships [3]. Presently, hydrogen sensing is necessary for areas like ammonia and methanol production, the hydration of hydrocarbons, the desulphurization of petroleum products and the production of rocket fuels [4]. Fuel cells can directly convert hydrogen into electricity by combining it with oxygen to produce water and no other harmful emissions. In the future hydrogen can be used to fuel vehicles, aircraft and provide power for our homes and offices [5].

1.2 NEED FOR LEAK DETECTION TAPES

Conventionally, hydrogen is detected using gas chromatography or mass spectrometry in the lab and using handheld sensors in the field. Hydrogen sensors are devices that detect hydrogen gas molecules and produce a signal with a magnitude proportional to the hydrogen gas concentration [6]. When the H_2 molecules interact with the sensing element of a hydrogen sensor, some of its properties such as refractive index, temperature, mass, electrical resistance and some mechanical properties are affected. These changes are then translated into, typically, an electrical signal by means of a transducer [7].

ISRO deals with liquid hydrogen carrying pipelines that stretch over several hundreds of meters. There is always the possibility of hydrogen leaking through the pipes, joints, bends or flanges. However, the handheld-instruments presently available are either unwieldy or costly or slow in terms of response time to hydrogen or cannot be used online. ***So, there is a need for an economical detection system that can be wrapped around such probable areas of hydrogen leakage and which can respond to leaks in around a second***.

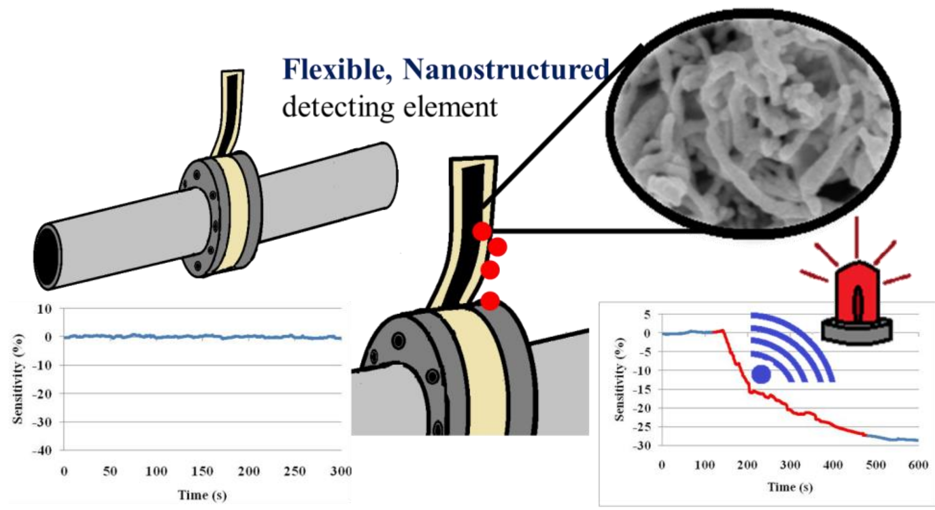


Figure 1: Schematic illustration of a proposed prototype of a leak detection tape wrapped around a flange for remotely monitoring [9] hydrogen leaks from pipelines.

In terms of contemporary technology being used, NASA employs a chemochromic tape, made from a mixture of PdO and TiO_2, that changes colour upon exposure to hydrogen. If pure hydrogen leaks, such a tape will change colour in a matter of about 10 s. If it is exposed to 1% H_2, then it has a response time of 3 min [8]. As such, there is ample scope for the development of an indigenous low-cost sensor/detector 'tape' that can respond to 1% H_2 in roughly a second. ***The goal of this project is the development of a low-cost, flexible hydrogen sensing tape for wrapping around liquid hydrogen carrying pipelines and flanges (Figure 1).*** Non-flammability, rapid response, and insensitivity to contaminants such as CO, CH_4, SO_2 etc. are desired performance characteristics.

In the ongoing project (ISTC0385), we have developed a process for uniformly coating nanoscale palladium overlayers on conductive silver nanowire networks that were formed using an inkjet printer. The preliminary response of these palladium nanostructures indicates the rapid response of the order of 30 s for 10% H_z environment, but their recovery is feeble. Given the low cost of manufacture, these films can serve as disposable leak detectors. However, extensive studies on optimising the response of different morphologies of nanostructured films have to be carried out, and we hope to achieve faster response times of the order of seconds. With these issues in mind, the specific objectives of this work were to 1) To design and optimise the morphology of silver@palladium nanostructures on polyimide tapes for leak detection along hydrogen carrying pipelines, and 2) To design and incorporate heaters for enhancing sensor recovery and hydrogen sensing performance

Approach

1) Silver@Palladium nanostructures will be formed on polyimide tapes by using the print-expose develop process and using the coffee-powder aided toner-recipe developed in our group.
2) Different morphologies and metal loadings will be tested for their electrical response to hydrogen environment to find the optimum morphology and loading for rapid leak detection.
3) Heating tapes, as well as printed heating pads, will be used to characterize the rate of hydrogen desorption and sensor recovery after exposure to hydrogen.

Previous work done in this area

Our group has developed expertise in fabricating silver nanowire networks or nanoparticle morphologies on both plastics as well as paper substrates. These have found applications as RF antennas, strain sensors, flexible electrodes for touch sensing, electroadhesive pads etc. In our ongoing STC project, we have developed techniques for forming a uniform coating of palladium on top of conductive silver nanostructures and characterized their hydrogen sensing performance using a home-built test set-up. We have also devised a simple way to enhance the adhesion of nanostructured thin films on plastic substrates.

Facilities Available and Equipment to be procured:

In our laboratory, we have the facility for fabricating metallic nanostructures, and a test set-up for characterizing their response to hydrogen leaks and flows. We also have access to CeNSE facilities for spectroscopic, material, and electrical characterization of nanostructures.

REFERENCES:

[1]: Jacobson, M.Z.; Colella, W.G.; Golden, D.M. Cleaning the air and improving health with hydrogen fuel-cell vehicles. Science 308 (2005); 1901-1905
[2]: (a) Liekhus, K.J.; Zlochower, I.A.; Cashdollar, K.L.; Djordjevic, S.M.; Loehr, C.A. Flammability of gas mixtures containing volatile organic compounds and hydrogen. J. Loss Prev. Process Ind. 13 (2000); 377-384 (b) Najjar, Yousef SH. "Hydrogen safety: The road toward green technology." Int. J. Hydrogen Energ. 38.25 (2013): 10716-10728

[3]: MAN Company, VorrichtungzurfortlaufendenBestimmung des Wasserstoffgehaltes in Gasgemischen, Patent DRP 165 349 (1904)
[4]: Hübert, T., Boon-Brett, L., Black, G., Banach, U. "Hydrogen sensors–a review." Sensor. Actuat. B:-Chem, 157.2 (2011): 329-352
[5]: Momirlan, M., Nejat Veziroglu, T. "The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet." Int. J. Hydrogen Energ. 307 (2005): 795-802.
[6]: Soundarrajan, P., Schweighardt, F. "Hydrogen sensing and detection." Hydrogen Fuel: Production, Transport, and Storage (2008): 495-534
[7]: (a) Buttner, William J., et al. Hydrogen Safety Sensor Performance and Use Gap Analysis: Preprint. No. NREL/CP-5400-68773. 2017. (b) Hübert, T., Boon-Brett, L., Buttner, W., Sensors for Safety and Process Control in Hydrogen Technologies (Vol. 14), CRC Press, 2016
[8]: (a) Roberson, Luke, et al. "Chemochromic Hydrogen Leak Detectors." KSC-13088, NASA Tech Brief (2009). (b) https://www.nasa.gov/offices/oct/feature/nasa-makes-leaks-easy-to-spot-on-tape, & https://www.nasa.gov/feature/hydrogen-detection-tape-saves-time-lives. Accessed on 21/7/2018
[9]: Lee. J, Oh,. J, Jang J. Wireless Hydrogen Smart Sensor Based on Pt/Graphene-Immobilized Radio-Frequency Identification Tag. ACS Nano, Vol 9, No 87783 (2015); 7790

Task schedule (Important Milestones for research reviews/completion of tasks – Please indicate Milestones that will be presented at Annual in House Seminar)

1st year: Fabricating Pd-Ag nanostructures on polyimide tapes that can be wrapped around pipelines. Optimization of palladium content for disposable leak detection tapes (response time of the order of seconds).

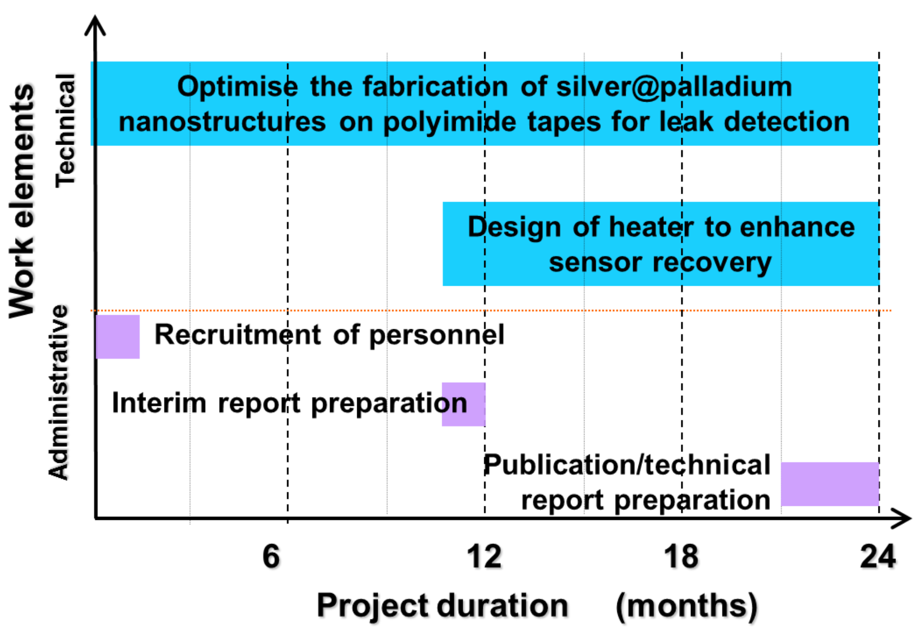
2nd year: Design and development of a sensor with an integrated heating element for enhancing recovery times.

Deliverables (To include the interim and Final Technical report)

1st year: Leak detection tape for field testing; Submission of interim technical report

2nd year: Palladium nanostructure-based hydrogen gas sensor response characterization at elevated temperatures; Submission of final technical report

Bar chart of Milestones for listed tasks



APPENDIX – D

1. List of projects (Title/Principal Investigator/Co-investigator/duration/amount) handled previously by IISc PI/Co-PI under STC.

   Nanostructured Chemoresistive Gas Sensor/Dr. Venugopal Santhanam/Dr. K. Nandakumar/2012-14/13.63,200

   Hydrogen Gas Sensor on Plastic Substrates/Dr. Venugopal Santhanam/Dr. K. Nandakumar/2017-19/14.88,100

2. List of publications arising out of these projects

   (a) Journals:

   S. K. Parmar, and V. Santhanam, " In situ formation of silver nanowire networks on paper", Curr. Sci. 107(2), 262-269 (2014).

   S Kumar, V Bhat, K J Vinoy, and V. Santhanam, "Using an Office Inkjet Printer to Define the Formation of Copper Films on Paper", IEEE Transactions on Nanotechnology, 13 (1), 160-164 (2014)

   P. Joshi and V. Santhanam, "Strain-sensitive inkjet-printed nanoparticle films on flexible substrates", IEEE Sensors Letters, 2 (1), pp.1-4 March (2018)

(b) Conference Proceedings:

(c) Technical Reports:

Nanostructured Chemoresistive Gas Sensor - ISTC/MCE/VS/286 (2014)