Platinum Overlayers on Nanostructured Electrodes

Other Technical Details – Platinum Overlayers on Nanostructured Electrodes

1. Origin of the Proposal: *(Maximum 1 page)*

Platinum and Platinum Group Metals (PGM) are the catalysts of choice for various electrochemical energy conversion processes involving Hydrogen Evolution/Oxidation (HER/HOR) and Oxygen Evolution/Reduction reactions (OER/ORR) [1]. However, the amount of platinum used in a Proton Exchange Membrane Fuel Cell (PEMFC) car is ~x6 used in the catalytic converters of combustion-powered cars[2]. This additional loading of a precious metal catalyst leads to a cost disadvantage and is one of the impediments to the mass adoption of hydrogen-powered cars.

The structural design of the electrocatalyst layer has evolved over decades to account for the need to transport heat, electrons and chemical reactants/products while providing a high surface area for conversion. Carbon-based supports are in vogue mainly for their high surface area, while the need for electrical conductivity and water management leaves scope for innovation. Furthermore, the durability of the PEMFCs in automotive applications is severely limited by the corrosion of the carbon support during start-up and shut-down cycles[3].

Presently, significant research is directed toward developing carbon-free nanostructured thin films as electrocatalyst layers for PEMFC applications[4]. Central to the success of such thin-film architectures is the formation of highly adherent platinum overlayers on conductive nanostructured substrates to minimize activation losses with load cycling attributed to ionomer adsorption and dissolution of catalyst particles[5].

In this context, our group is working to develop scalable routes for fabricating nanoporous, electrically conducting, electrocatalytically active thin films that meet the activity and durability targets for PEMFCs. Previously, we utilised gold@platinum core-shell nanoparticle self-assembly[6] in conjunction with RF plasma treatment[7] to form such thin films. However, this process is limited to batch fabrication. Recently, we have developed a scalable strategy based on inkjet printing to form thin films of silver nanostructures on any desired substrate[8]. Presently, we are investigating the capability to adopt electrochemical routes to develop durable platinum overlayers on nanoscale gold/silver films[9] During the investigations, several scientific and technical challenges have been identified and have led to this project proposal.

In particular, the specific objectives of this proposal are:-

1. **To develop a molecular-level understanding of the process of platinum overlayer formation**
2. **To fabricate platinum overlayers on nanostructured metallic thin films in a scalable flow cell configuration**
3. **To characterize the electrocatalytic performance of the fabricated films at the lab-scale (~1 cm^2 area) and a single-cell level (~25 cm^2 area)**

2. Review of the status of Research and Development in the subject

2.1 International Status: *(Maximum 2 pages)*

The need for highly durable electrocatalysts based on novel electrode designs to overcome cost barriers for mass-adoption of PEMFC automotives has been well documented in several reviews[4,5,10,11] The US DOE performance targets for durability (< 40% loss in activity after 30,000 start-stop cycles equivalent to 1,50,000 mileage) and mass activity (0.44 A/mg_{PGM} at 0.1 mg_{PGM}/cm^2.) of PEMFC electrocatalysts are the drivers of research and innovation in this area. The various approaches and strategies pursued by several leading research groups in the US are documented in the annual review meeting reports available at https://www.hydrogen.energy.gov/annual_review.html. In the following, I will focus on key publications on the fabrication of platinum overlayers (a few atomic monolayers), which is pertinent to the strategy outlined in this proposal to meet activity and durability performance targets.

Platinum overlayers on metal substrates exhibit enhanced activity, attributed to ensemble and ligand effects[12,13], making them appropriate candidates for meeting platinum loading targets for fuel-cell applications. Such overlayers also maximize platinum utilisation.

Colloidal phase synthesis of platinum overlayers on nanoparticles as core-shell particles is one such approach that has been pursued by many groups[14–21]. However, this does not address the carbon corrosion issue.

3 M has proposed Nano-Structured Thin Film (NSTF) architecture for alleviating issues associated with carbon corrosion[22–24]. The fabrication involves the formation of an organic whisker-like nanostructure by sublimation and subsequent sputter coating of the "non-corrodible" substrate with a thin metallic film (~50-100 nm thick) of desired composition and layers. These catalysts have enhanced durability, adequate power density and exceptional mass activity[25–27] for automotive applications. However, using a vacuum-based sputtering process poses techno-economic hurdles for scaling this process up to commercial-scale manufacturing.

Electrochemical Atomic Layer Deposition (eALD) utilises surface-limited reactions under electrochemical conditions to deposit Pt overlayers on an electrode[28]. Typically, these surface-limited reactions involve UnderPotential Deposition (UPD). UPD is about one atom thick layer deposited at a potential that is above (in IUPAC convention, but "under" in US convention that uses -ve scale) the value predicted by Nernst equation[29]. The stabilisation provided by the heteroatomic interactions compared to the self-interactions of the two components is the reason behind this shift in deposition potential[29]. Typically, these layers are self-limiting to one atomic layer at this underpotential and are unaffected by surface heterogeneities[30,31].

eALD of platinum overlayers on conductive substrates involves using a sacrificial layer, as the cohesion energy of platinum is very high compared to adhesion on a heterosurface[14–16,28,30,32–34]. The properties of the sacrificial layer are used to control the extent of surface coverage. As such, copper and lead are two of the most commonly used

sacrificial layers, with lead providing a more uniform coverage[35–45]. The platinum atomic overlayer is formed by Galvanic displacement of the sacrificial layer in a subsequent step.

In the recent past, two groups have utilised pulsed electrodeposition with hydrogen adsorption as a tool to promote the 2D growth of platinum as atomic overlayers on conductive substrates. The "Self-Terminating ElectoDeposition" (STED) technique involves the stepping of potential from a value at which adsorbed platinum chloride (precursors for platinum deposition) is stable (~0.87 V_{RHE}) into a zone where the HER reaction intermediates dominate the electrocatalyst surface (~-0.33 V_{RHE}) to form quasi 2D monolayers of platinum on flame-annealed gold surfaces (~550 ng/cm^2)[46]. Subsequently, this technique has been extended to "reactive" substrates such as Ni, Co, Fe[47] and oxides such as TiOx[48]. However, the platinum adlayer is no longer limited to atomic thickness on these substrates. Instead, "approximate" monolayers of nanoparticulate deposits are formed. The differences in deposit structures are variously attributed to the changes in the rates of platinum chloride reduction and surface termination by hydrogen adsorption on these substrates. The pH dependence of the onset of electrodeposition points to the role of adsorbed hydrogen as an intermediate in the deposition. However, there is no clear demonstration of the rate-controlling steps in these pulsed electrodepositions.

In a similar vein, the Surface limited redox reaction (SLRR) cycle has been extended by a pulsed electrodeposition route (from 0.82 V_{RHE} to 0.07 V_{RHE}) to use underpotential deposited hydrogen (H_{upd}) as the "sacrificial" layer to form platinum/ palladium overlayers[45,49] on platinum-plated substrates. The deposition corresponds to about ½ a monolayer of platinum per cycle, supporting the claim of platinum chloride being reduced by adsorbed H_{upd}.

Despite the striking similarities between the two pulsed electrodeposition approaches, the quartz crystal microbalance profiles indicate a sharp transition in mass change for the STED protocol, while the mass change profile is gradual in the SLRR approach. These facts are intriguing and beg clarification if the process is to be scaled up for mass manufacturing.

The total number of fuel-cell cars sold over the past decade is of the order of a few thousand, while the global auto sales are of the order of 80 lakhs/year[48]. If all of this demand is to be met by PEMFCs, then the platinum loading per vehicle needs to be a few g/vehicle (similar to that used in exhaust catalytic converters). Such a reduction in platinum loading calls for the development of scalable protocols for forming platinum overlayered electrocatalysts. Although pulsed electrodeposition based approaches have emerged as a likely candidate to carry out eALD in a flow-setup[50], the lack of understanding of the deposition process has led to irreproducibility being attributed to the "cell constant"[47]. Based on our ongoing research activity, we feel there is ample scope for improved understanding and potential innovations to address these challenges.

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2.2 National Status: *(Maximum 1 page)*

Our group at IISc has been working on platinum overlayer based electrocatalysts for the last decade. Our initial efforts were based on bottom-up self-assembly of gold@platinum core-shell nanoparticles[6] and subsequent plasma treatment[7] to form conductive, nanoporous, electrocatalytically active thin films. In the recent past, we have studied the pulsed electrodeposition process and characterised the durability of the platinum overlayers thus formed.[9]

Prof. Raj Pala's group[51] (Dept. Chemical Engg, IIT-Kanpur) has used molecular modelling tools in conjunction with experiments to understand the performance of ruthenium oxide overlayers on various supports to identify the overlayer-substrate combination with the best activity possible as per the peak of the corresponding Sabatier relationship.

Prof. R. Kothandaraman's group (Dept. of Chemistry, IIT-Madras) has evaluated the durability of platinum catalysts on porous carbon supports derived from tamarind seeds in single cell configuration[52]. They determined the effect of N-atom coupling to be advantageous for hindering the corrosion of the porous carbon support.

Prof. Pravin Ingole's group[53] (Dept. of Chemistry, IIT Delhi) has electrodeposited $_{Pt3Co}$ layers directly on carbon to avoid adsorbed Nafion ionomer induced mass transfer resistance to oxygen transport and enhance the activity of the oxygen reduction reaction.

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Prof. Abhijit Chatterjee's group[54] (Dept. Chemical Engg, IIT-Bombay) has studied the kinetic stability of platinum skin overlayers on gold nanoparticles using Monte Carlo simulations and found that the more stable configuration is of gold creeping on top with the platinum forming subsurface layers.

Dr Rajalakshmi's group (CFCT-ARCI, Madras) has developed a patent-pending technology for synthesizing nitrogen coupled durable carbon supports for platinum electrocatalysts that exhibit strong support metal interaction; hence enhanced durability.

In summary, this brief overview of the contribution of Indian scientists covers only a small fraction of the spectrum of researchers identified in the recent report from SERB on hydrogen economy available at
https://dst.gov.in/collation-indias-hydrogen-fuel-cells-research-status-launched.
Indian scientists have played a significant role in developing various carbon supports with enhanced durability. Apart from a few recent studies on catalytically active overlayers, the scaled-up synthesis of platinum overlayers on carbon-free supports is yet to be studied extensively.

2.3 Importance of the proposed project in the context of current status *(Maximum 1 page)*

Given the high environmental costs of using high-energy/power density fossil fuels for transportation, the switch to a hydrogen-powered fuel cell model seems to be one of the better choices. To achieve this at scale, the extent of platinum utilised in electrocatalyst layers needs to be of the order of 1g/car (700 kWh) to avoid creating another environmental disaster by mining the planet to "death" for supplying these catalytic materials (~ 100 tons/year). The recently established pulsed electrodeposition protocols are the most promising routes to scalably produce atomic-scale platinum overlayers that are durable and active.

This proposal intends to build on our recent findings on pulse electrodeposited platinum overlayers and deepen our understanding of the critical variables involved. These studies will help us identify appropriate modified protocols for repeatable fabrication of platinum overlayers on gold/silver thin films. Based on these modifications, we intend to adapt them to form platinum overlayers on conductive nanostructured metallic thin films formed by inkjet printing. Furthermore, we will be adopting these protocols to a flow cell configuration as these offer the possibility of roll-to-roll processing, and large-scale additive manufacturing of ultra-low platinum loaded electrocatalyst layers. We will also study the prospects of recycling the electrolyte solutions to ensure maximum precious metal precursor solution utilisation. Such studies are required to develop the know-how for translating this promising lab-scale technique to largescale production.

2.4 If the project is location specific, basis for selection of location be highlighted:

-NA-

3. Work Plan:

3.1 Methodology: *(Maximum of 5 pages)*

(It should contain all the details of how each of the objectives will be addressed. This section must be detailed and have clear plans, not vague and generalized statements. It should have several schemes, tables, figures, equations etc. in addition to text, explanation and justification of why the project research plan will work)

1. *Electrodeposition on metallic thin films*

A systematic effort in a lab-scale three-electrode electrochemical setup will be undertaken to study the effect of platinum precursor concentration and the potential limits to mitigate the prospects of Galvanic displacement/side reactions while immersed in the electrodeposition bath. These experiments will be carried out at the beaker-scale initially. We also plan to carry out investigations wherein extra precautions are maintained (in the form of purging the electrolytes with inert gases) to avoid the leakage and subsequent oxygen dissolution. If found necessary, even the solutions used for rinsing will be purged to prevent local pitting corrosion observed in preliminary investigations. We hope to identify optimal conditions for fabricating platinum overlayers at the atomic scale on thin silver films comparable to the durable films fabricated on gold.
Several preliminary findings, such as the deposition of thicker films (equivalent to 10 atomic layers) on silver as compared to the single atomic layer thick films formed on gold; the inability of the thicker platinum films to prevent corrosion of the underlying silver; and the formation of ultrastable silver=platinum alloy skins need to be investigated more thoroughly. We plan to vary the speed of potential pulsing and the potential window as well as the instance of precursor addition to control the overlayer formation.
These experiments will enhance the molecular-level understanding of the overlayer formation process and help us identify suitable "terminating" agents to avoid bulk deposition of platinum.

2. *Electrodeposition in a flow cell configuration*

The ability to scale up this platinum overlayer electrodeposition will depend on the ability to recycle the reagents/electrolyte solutions while avoiding oxygen dissolution. Flow cell configurations[50] *can minimise the amount of electrolyte used during deposition and maintain them in a closed-loop. Such flow cell configurations can potentially be integrated with roll-to-roll processing of the thin film substrate, which will be critical for scaling up. We have requested funds to purchase such an electrochemical flow cell with appropriate peristaltic pumps for studying this aspect.*

3. *Ex-Situ electrochemical activity and durability testing of platinum overlayer samples*

We plan to use the existing facility at IISc, which is designed for carrying out prolonged ex-situ durability experiments (over days) without introducing any artefacts. We have spent a significant effort over the last two years in developing the skillsets required[55].

4. *Scaling up batch/flow-cell process for fabrication of large-area (>25 sq.cm) substrates*

We will initially use small area substrates (~1 sq. cm). After we understand the nature of the dynamics of electrodeposition (double-layer structure alteration dynamics is envisaged to be the key as platinum precursor and protons have to enter and leave at appropriate times), we will fabricate a large-area deposition chamber to ensure that the dynamics are fast (by appropriately configuring inlets and outlets). Both planar and cylindrical configurations are proposed to be used. Planar structures may be easier to fabricate, while we hope to utilise the capabilities of the upcoming machining facility at IISc to fabricate a tube-like format for deposition onto our nanostructured substrates. It will first be used in batch mode, and then we plan to adapt it to a flow-cell configuration.

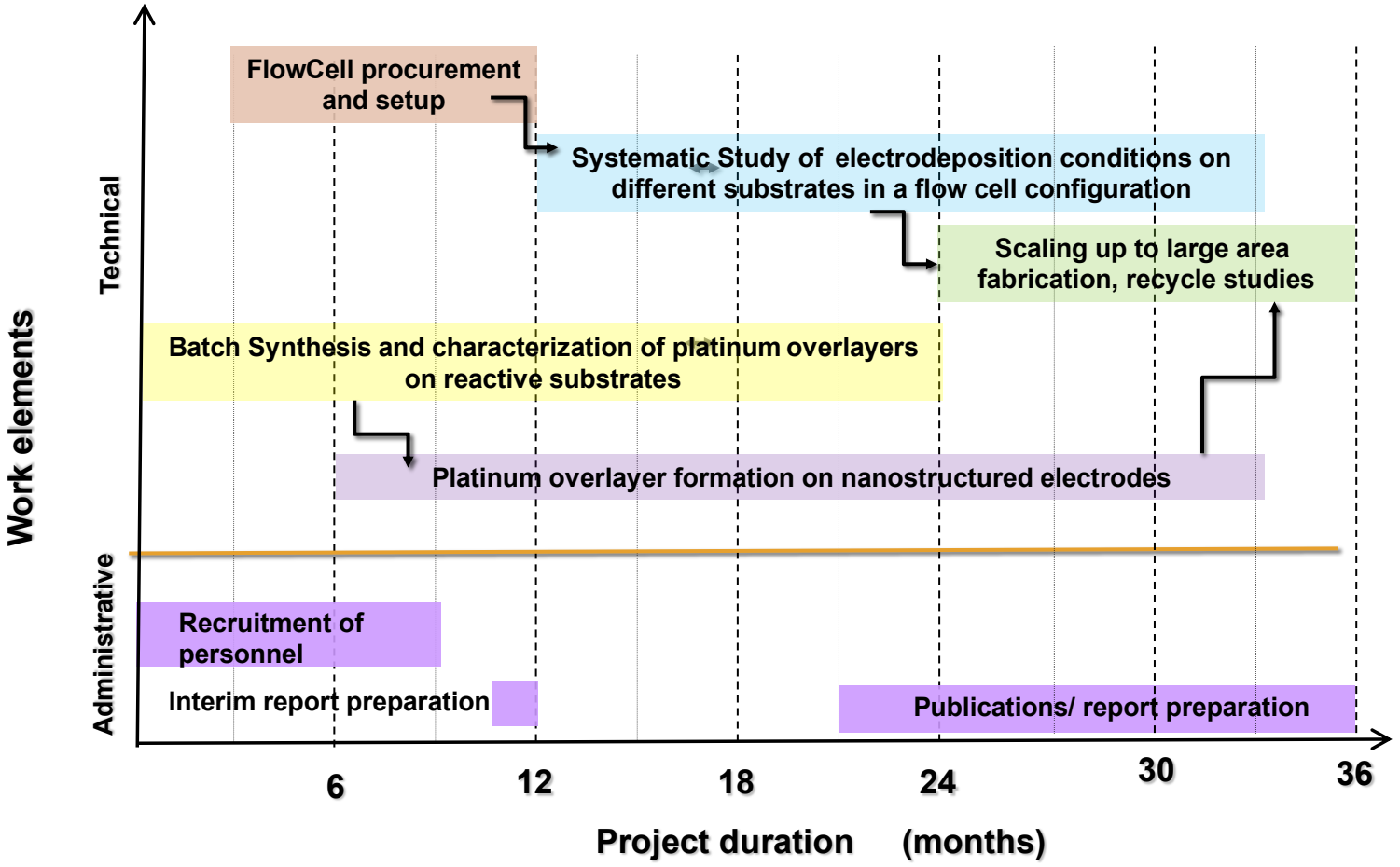
As substrates, we will initially use thin films of various metals, mainly gold, silver and their alloys, as substrates. Once we identify the optimal conditions for thin films, we will adapt the process to plate onto inkjet-printed silver nanostructures. We envisage some issues with the need to adjust the electrolyte composition lower to avoid Galvanic erosion over the longer time periods expected for plating such nanostructures.

5. *Performance evaluation in a fuel cell testing station*

After the large-area substrates have been successfully electrodeposited, we plan to print the silver nanostructures on Nafion membranes and then electrodeposit platinum overlayers using the developed flow-cell configuration. After that, we need to optimize various aspects of the cell configuration, like the use of appropriate surface modification agents, combining with a Gas Diffusion Layer having suitable porosity etc., to maximise the power output. These preliminary findings will then form the basis of further research into the development of this method of fabricating electrocatalyst layers to larger scales.

The methodology envisaged involves the optimization of various aspects that will be carried out concurrently by Research students, Project Assistants, Masters students and summer interns. As such, we expect to follow the time schedule presented in the next section.

3.2 Time Schedule of activities giving milestones through BAR diagram. (Maximum 1 page)



3.3 Suggested Plan of action for utilization of research outcome expected from the project. *(Maximum ½ page)*

The outcomes of this research will lead to processes for manufacturing durable and ultralow Pt loaded nanostructured electrodes for PEMFC applications. The training of skilled human resources will be of import for the advancement of the hydrogen economy in India.

The research output will be disseminated via journal publications and conferences and will lead to collaborative opportunities with industry partners to advance the technology further. If the scale-up is successful, then there is a possibility of spinning off an OEM manufacturing unit for low-Pt loaded electrodes.

3.4 Environmental impact assessment and risk analysis. *(Maximum ½ page)*

The project involves using standard gases and chemicals that will be handled and disposed of as per the safety norms of IISc (https://olseh.iisc.ac.in/).
The research outcomes will benefit the vision of a “Hydrogen-Economy” by providing a commercially viable pathway for mass adoption of PEMFC automobiles.

4. Expertise:

4.1 Expertise available with the investigators in executing the project: *(Maximum 1 page)*

Our group has expertise in the scalable synthesis of metallic nanoparticles for energy and sensing applications. In particular, we developed a self-assembly based process for fabricating ultra-low Pt loaded, nanostructured, electrically conducting, carbon-support free catalytic layers for PEMFC applications[56,57]. That research resulted in a deeper understanding of the requirements of the field. It made the need to search for a simpler process to fabricate platinum overlayers on nanostructured, conductive supports. This search led to developing a more straightforward method for fabricating silver-based conductive nanostructures using an inkjet printer (Media Highlight-Science Monitor, DD Rajya Sabha TV, 08/08/2015). The immediate outcomes of this process development work have been products such as flexible SERS sensors for pesticide detection, hydrogen leak detectors, flexible RF antennas, and electroadhesive pads.

In the recent past, we have developed the expertise and skill[55] required to fabricate platinum atomic layers by using electrodeposition and modified chemistries to form ultra-low loaded Pt electrocatalyst layers with enhanced durability[9] and activity on nanoscale thin films of gold and silver. Preliminary investigations on adapting this process to form durable electrocatalyst layers on silver nanostructures formed by inkjet printing are promising. This proposal aims to extend these efforts to develop durable, ultra-low Pt loaded electrocatalyst layers for PEMFC applications.

4.2 Summary of roles/responsibilities for all Investigators:

S. No.	Name of the Investigators	Roles/Responsibilities
1.	S. Venugopal	PI/Plan and implement project

4.3 Key publications published by the Investigators pertaining to the theme of the proposal during the last 5 years

K. Agrawal, A.A. Naik, S. Chaudhary, D. Parvatalu and V. Santhanam, "Prudent Practices in Ex-Situ Durability Analysis Using Cyclic Voltammetry for Platinum-based Electrocatalysts", Chem-Asian J 16(21), 3311-3325 (2021)

K. Agrawal, S. Chaudhary, D. Parvatalu, and V. Santhanam "Durability of Platinum Overlayers formed By Self-Terminating Electrodeposition". ECS Transactions, 104(8), 379 (2021). https://doi.org/10.1149/10408.0379ecst

A. Kumar and V. Santhanam, "Paper Swab based SERS Detection of Non-Permitted Colourants from Dals and Vegetables Using a Portable Spectrometer", Anal. Chim. Acta 1090, 106–113 (2019)

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

P. Joshi and V. Santhanam, "Inkjet-based fabrication process with control over the morphology of SERS active silver nanostructures", Ind.Eng.Chem.Res. 57 (15), 5250–5258 (2018)

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13. Deng, Y. J., Tripkovic, V., Rossmeisl, J. & Arenz, M. Oxygen Reduction Reaction on Pt Overlayers Deposited onto a Gold Film: Ligand, Strain, and Ensemble Effect. *ACS Catalysis* **6**, 671–676 (2016).
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5. List of Projects submitted/implemented by the Investigators

5.1 Details of Projects submitted to various funding agencies:

S. No	Title	Cost in **Lakh**	Month of submission	Role as PI/Co-PI	Agency	Status
1	Catalysis for a Circular BioEconomy	₹ 526.36	Dec 2021	PI	SERB-Specoal call—Circular Economy	Submitted
2	Flexible MetaSurface Antennas for Mobile VSAT Applications	₹ 12	Nov 2021	PI	TCS-IISc Innovation Cell	Accepted for funding, Legal Negotiations on IPR ongoing

5.2 Details of Projects under implementation:

--NA--

5.3 Details of Projects completed during the last 5 years:

S. No	Title	Cost in Lakh	Start Date	End Date	Role as PI/Co-PI	Agency
1	Leak Detection Tapes for Hydrogen Pipelines	₹ 15.6 Lakhs	01/04/2019	31/03/2022	PI	ISTC-ISRO
2	Printed Electrocatalyst Layers for PEMFC/DMFC	₹ 27.4 Lakhs	18/07/2019	31/03/2022	PI	OECT-ONGC
3	Nanostructured Metallic Thin Films (NMTF) for Sensing and Energy Conversion	₹ 49.6 Lakhs	20/10/2017	31/03/2021	PI	SERB
4	Hydrogen gas sensor on flexible substrates	₹ 14.7 Lakhs	01/04/2017	31/03/2019	PI	ISTC-ISRO

6. List of facilities being extended by parent institution(s) for the project implementation.

6.1 Infrastructural Facilities

Sr. No.	Infrastructural Facility	Yes/No/ Not required Full or sharing basis
1.	Workshop Facility	SHARING BASIS
2.	Water & Electricity	YES
3.	Laboratory Space/ Furniture	YES
4.	Power Generator	SHARING BASIS
5.	AC Room or AC	NOT REQUIRED
6.	Telecommunication including email & fax	YES
7.	Transportation	NOT REQUIRED
8.	Administrative/ Secretarial support	SHARING BASIS
9.	Information facilities like Internet/Library	YES
10.	Computational facilities	SHARING BASIS
11.	Animal/Glass House	NOT REQUIRED
12.	Any other special facility being provided	SOPHISTICATED ANALYSIS/ INSTRUMENTAL FACILITIES ON PAYMENT BASIS

6.2 Equipment available with the Institute/ Group/ Department/Other Institutes for the project:

Equipment available with	**Generic Name of Equipment**	**Model, Make & year of purchase**	**Remarks including accessories available and current usage of equipment**
PI's group	3D Printer Electrochemical Workstation	WOL3D ENDER 3 MODEL, 2021 Origalys Electrochemical workstation.	Used for forming Metal/Metaloxide patterns on various substrates For electrochemical characterization and platinum overlayer deposition
PI's Department	Fuel Cell Testing Station		For performance characterization of platinum overlayer coated nanostructured electrodes
PI's Institute	Structural, Material and spectroscopic Characterization facilities		Common faciities available on payment basis

7. Name and address of experts/ institution interested in the subject / outcome of the project.

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