Annexure-I

Printed Electrocatalyst Layers for PEMFC/DMFC

PROJECT PROPOSAL

Submitted to

ONGC Energy Centre Trust

By

Dr VENUGOPAL SANTHANAM
Department of Chemical Engineering
Indian Institute of Science
Bangalore 560 012
February 2019

1. **Project Title:** Printed Electrocatalyst Layers for PEMFC/DMFC
2. **Duration in months:** 18
3. **Total Estimated Budget:** ₹ 24 13 353
4. **Principal Investigator:** Dr Venugopal Santhanam

   Designation: Assistant Professor

   Department: Chemical Engineering

   Institute Name: Indian Institute of Science

   Address: Lab 2A, Department of Chemical Engg, IISc-Bangalore, 560012

   Telephone: 80-22933113, 9448833358

   Fax: 80-23608121

   E-mail ID: svgpal@iisc.ac.in
5. **Co-Investigator:**

   Designation:

   Department:

   Institute Name:

   Address:

   Telephone:

   Fax:

   E-mail:

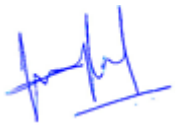
SECTION - A

Certificate from the Principal Investigator and Collaborating Institute/ Organization

Project Title: Printed Electrocatalyst Layers for PEMFC/DMFC

I am submitting the above-titled project proposal to OECT as a collaborative research/technology development project.

1. I agree to abide by the terms and conditions of OECT for supporting research/technology development projects including the posting of OECT manpower in the project team.
2. I have not submitted the project proposal elsewhere for financial support.
3. I have requested for funds for the items, which are not available with the institution for the proposed work and are absolutely essential.
4. I will not proceed on long term/ study leave/deputation during the period of project implementation, without prior intimation to OECT.



Place: Bangalore **(Name & Signature of Principal Investigator)**
Date: 05/02/2019

Endorsement by the Head of the Institution/Organisation:

Certified that Project Proposal entitled "Printed Electrocatalyst Layers for PEMFC/DMFC " is prepared by Dr. Venugopal Santhanam and has not been submitted to any other institution/organisation for funding. This institute/organisation will provide necessary regular staff, administrative support and required infrastructure facilities for the project work and such facilities have not been requested in the proposal. The institute/organisation will ensure compliance of the terms and conditions of project funding by OECT and other conditions governing the implementation of the project.

Place: Bangalore **(Name, Signature & Seal**
Date: **of Head of Institute/Organization)**

SECTION – B

1.0 Project Title: Printed Electrocatalyst Layers for PEMFC/DMFC

2.0 Project Type (Choose from the following):

- Basic Research
- **Lab Scale Product /Process/Technology Development ✓**
- Product/Process/Technology Improvement
- Pilot Scale Development
- Pre-Industry Model Development
- Technology Demonstration/Validation
- Field Implementation/Trials of Product/Process/Technology developed Others

3.0 Introduction and Review of Literature:

Polymer Electrolyte (or proton exchange) Membrane fuel cells (PEMFC) and Direct Methanol fuel cells (DMFC) are energy-efficient alternatives to combustion engines for automotive(Mark K Debe 2012) and mobile/remote applications,(Joghee et al. 2015; Sundarrajan, Allakhverdiev, and Ramakrishna 2012) and are on the cusp of mass-production. Fuel cells directly convert the bonding energy of the fuel into useful work and are significantly more efficient than combustion engines. However, considerable innovation is required to achieve US Fuel Cell Technologies Office (FCTO - Multi-Year Research, Development, and Demonstration Plan) targets of cost (platinum group metal – PGM loading < 125 $\mu g/cm^2$), durability (<40% loss of activity after 30k cycles), and performance (0.44 A/mg_{pt} @0.9 V).

Significant advances have been made in PEMFC/DMFC system design over the last three decades in terms of cost-reduction and structural design.(Gasteiger et al. 2005) The membrane electrode assembly (MEA), especially the electrode, is considered as 'the heart' of a fuel cell and is designed to accommodate constraints imposed by the cost of platinum used for electrocatalysis, as well as the need for efficient transport of electrons, reactants and heat. Consequently, the structure and composition of the 'electrode' has been significantly altered over the years, from utilizing platinum black films with a platinum loading of 10 g_{pt}/cm^2 in 1970s to present-day platinum/PGM nanoparticle coated carbon black particles (Pt/C) that use about 0.3 mg_{pt}/cm^2.(Costamagna and Srinivasan 2001) The use of highly-dispersed nanoparticles on carbon black particles enables substantial gains in surface area for a given mass of catalyst, but concomitant durability problems due to carbon support corrosion and loss of surface area under PEMFC working conditions,(Cao, Wu, and Cao 2014; Ferreira et al. 2005; Paddison and Gasteiger 2013) especially during start-up or shut down cycles have led to renewed interest in carbon-free nanostructured electrodes,(Antolini and Perez 2011) which employ a thin coating of platinum or PGM based catalytic layer on a mesostructured conductive support.(van der Vliet et al. 2012; Inaba et al. 2015; M. K. Debe 2013; Ge et al. 2009; Biener et al. 2011; Cheng et al. 2015; Liu et al. 2009; Kloke et al. 2012; Alia et al. 2010; Kloke et al. 2011) Such thin film architectures can also lead to reductions in platinum loadings to about 0.05 mg/cm^2,(Zeis et al. 2007),(Tiwari et al. 2018) while reducing surface area losses due to nanoparticle agglomeration and preventing corrosion of the underlying substrate.(Mark K. Debe et al. 2006)

3.1 Current status of Work being done in other Institutions and Industries in the country:

Lab-scale colloidal synthesis of catalysts for PEMFC applications has been extensively studied by various groups in India over the last decade. (Ghosh et al., 2013; Sahoo et al., 2015; Baronia et al., 2018; Sha and Badhulika, 2018; Radhakrishnan and Sandhyarani, 2019) A brief account of literature reports from Indian Institutions over the last 5 years on ORR/MOR electrocatalysts with low PGM content or enhanced durability is provided herein.

A simple, scalable, single-step synthesis method was adopted to develop platinum-free, palladium-cobalt alloy supported on nitrogen-doped reduced graphene oxide (Pd_3Co/NG) nanocomposite.(Chandran, Ghosh, and Ramaprabhu 2018) The low value of the reported maximum power density of 0.07 W/cm^2 using 0.5 mg/cm^2 of catalyst highlights the difficulty of platinum-free strategies for fuel cell electrocatalysis. A self-limiting electroless shell deposition method for synthesizing Pt overlayer coated Pd/C catalysts for ORR was demonstrated.(Mahesh and Sarkar 2018) Platinum nanoparticles deposited on Mn, Fe and Co based spinal oxides, synthesized by co-precipitation method followed by sintering at high temperature, exhibited high ECSA value of 132 m^2/g_{pt}, a maximum power density of 0.7 W/cm^2 in a fuel cell configuration, specific activity of 0.2 A/mg_{pt}, and a 17% loss of activity after 1000 cycles.(Mohanraju et al. 2017) Pt/V-TiO2 nanocomposite catalyst, prepared via a sol-gel and microwave assisted chemical reduction route, were found to lose only 20% activity after 6000 cycles of accelerated stress testing.(Bharti and Cheruvally 2017) Nano ceria supported nitrogen doped graphene as a highly stable and methanol tolerant electrocatalyst for oxygen reduction was synthesized using a single-step solvothermal process.(Soren et al. 2016) A ~30 % enhancement of the durability of Pt/C catalyst on oxygen and nitrogen functionalized nanocarbon supports was attributed to the presence of large amount of pyrrolic nitrogen and highly oriented graphitic nature of the catalyst supports.(Karthikeyan et al. 2015) They reported ECSA of 24 m^2/g_{pt} and a maximum power density of 0.4 W/cm^2.(Puthusseri and Ramaprabhu 2016) The use of ascorbic acid as a functionalizing agent to enhance anchoring of Fe_2O_3-Pt core-shell as well as reducing and capping agent was studied (Dhavale and Kurungot 2012).

3.2 Current status of work being done on an International scale:

The DOE Merit Review meeting, 2018 provides an excellent overview of the current status of research directions aimed at reducing the cost and improving the durability of catalysts while maintaining high specific activity. The multi-pronged approach being pursued in catalyst development includes theoretical computations aimed at understanding and providing material leads for circumventing the sluggishness of ORR kinetics, (Solomon and Stahl 2018) developing strategies for synthesizing nanomaterials with tailored morphology, such as nanoframes, core-shell etc. to enhance intrinsic activity.(Stamenkovic et al. 2017; Li et al. 2016) Interestingly, Nanostructured thin film catalysts were found to exhibit a x8 fold increase in activity over polycrystalline platinum facets. These approaches are capable of addressing some of the DOE targets in terms of durability or activity or PGM content at the lab-scale (https://www.energy.gov/eere/vehicles/annual-merit-review-presentations), but several obstacles need to be surmounted prior to scaling-up these findings. Amongst the several approaches, nanostructured thin film architecture for electrocatalyst layer is a promising route for cost-effective scaling up to manufacturing scale.

Nanostructured thin film catalyst layers have been deposited either using top-down approaches such as sputter deposition(van der Vliet et al. 2012; Ge et al. 2009)or atomic layer deposition (ALD)(Inaba et al. 2015) onto organic mesostructures that are *a priori* coated with a conductive layer or bottom-up techniques that utilize nanoporous metallic films, formed by dealloying, as a conductive substrate onto which thin platinum layers are deposited by chemical(Zeis et al. 2007) or electrodeposition(Kloke et al. 2012; Alia et al. 2010; Kloke et al. 2011; McCurry et al. 2011)routes. The reported values of the electrochemically active surface areas (ECSA) for thin film nanostructured catalyst layers are much lower than that of conventional Pt/C layers, but their performance under fuel cell test conditions are equivalent to that of Pt/C layers, and this is attributed to enhanced specific activity associated with bulk-like polycrystalline grains as well as enhanced electrical conductivity of the catalyst layer.(M K Debe 2010) Presently, the thicknesses of the metallic films used in such electrodes are of the order of 100 nm to provide macroscopic uniformity of coating and ensure electrical connectivity. Despite these advancements, there is ample scope for developing simpler and cost-effective additive fabrication processes and novel designs of the electrocatalyst layer to further reduce platinum/PGM loading of thin film nanostructured electrodes.

3.3 Details of previous work and ongoing work of PI and Institute/Organisation in this field and expertise available with PI/Group/Institution/Organisation:

Our group has developed a simple process for fabricating nanostructured metallic thin films on paper and plastic substrates using a simple desktop inkjet printer (Media Highlight-Science Monitor, DD Rajya Sabha TV, 08/08/2015). The process chemistry is based on the well-developed silver halide chemistry used in the field of photography. [1] Apart from this, we fabricated and characterized the electrochemical performance of ultralow-platinum loading (<5 μg/cm^2) electrodes for fuel cells using self-assembled monolayers of Au@Pt nanoparticles as the building blocks. [2,3] Therein, we have developed expertise in handling and characterizing electrodes for PEMFC applications. Over the past year, Mr Khantesh Agrawal has successfully adapted the printing process to Nafion membrane to form a nanostructured porous conductive layer. [3] He is currently involved in optimizing conditions for Platinum overlayer deposition onto silver nanowires.

1. S. K. Parmar, and V. Santhanam, " in situ formation of silver nanowire networks on paper", Curr. Sci. 107(2), 262-269 (2014)
2. I. Banerjee, V. Kumaran, and V. Santhanam, "Synthesis and Characterization of Au@Pt Nanoparticles with Ultrathin Platinum Overlayers", J. Phys. Chem. C , 119 (11), 5982–5987 (2015)
3. I. Banerjee, V. Kumaran, and V. Santhanam, "Fabrication of Electrodes with Ultralow Platinum Loading by RF Plasma Processing of Self-Assembled Arrays of Au@Pt Nanoparticles", Nanotechnol. 27, 305401 (2016)
4. K. Agrawal, “Printed Electrodes for PEMFC”, M Tech Report, IISc, 2018

3.4 Patent search reports and the details of patents filed and granted to the PI/institute in the related field(s) if any: **-NA-**

References:

Alia, Shaun M., Gang Zhang, David Kisailus, Dongsheng Li, Shuang Gu, Kurt Jensen, and Yushan Yan. 2010. "Porous Platinum Nanotubes for Oxygen Reduction and Methanol Oxidation Reactions." *Advanced Functional Materials* 20 (21): 3742–46. https://doi.org/10.1002/adfm.201001035.

Antolini, Ermete, and Joelma Perez. 2011. "The Renaissance of Unsupported Nanostructured Catalysts for Low-Temperature Fuel Cells: From the Size to the Shape of Metal Nanostructures." *Journal of Materials Science* 46 (13): 4435–57. https://doi.org/10.1007/s10853-011-5499-3.

Baronia, Richa, Jyoti Goel, Jyoti Kaswan, Ajay Shukla, Sunil K. Singhal, and Surinder P. Singh. 2018. "PtCo/RGO Nano-Anode Catalyst: Enhanced Power Density with Reduced Methanol Crossover in Direct Methanol Fuel Cell." *Materials for Renewable and Sustainable Energy* 7 (4): 27. https://doi.org/10.1007/s40243-018-0134-8.

Bharti, Abha, and Gouri Cheruvally. 2017. "V-Doped TiO2 Supported Pt as a Promising Oxygen Reduction Reaction Catalyst: Synthesis, Characterization and in-Situ Evaluation in Proton Exchange Membrane Fuel Cell." *Journal of Power Sources* 363 (September): 413–21. https://doi.org/10.1016/J.JPOWSOUR.2017.07.111.

Biener, Monika M, Juergen Biener, Andre Wichmann, Arne Wittstock, Theodore F Baumann, Marcus Bäumer, and Alex V Hamza. 2011. "ALD Functionalized Nanoporous Gold: Thermal Stability, Mechanical Properties, and Catalytic Activity." *Nano Letters* 11 (8): 3085–90. https://doi.org/10.1021/nl200993g.

Cao, Minna, Dongshuang Wu, and Rong Cao. 2014. "Recent Advances in the Stabilization of Platinum Electrocatalysts for Fuel-Cell Reactions." *ChemCatChem* 6 (1): 26–45. https://doi.org/10.1002/cctc.201300647.

Chandran, Priji, Arpita Ghosh, and Sundara Ramaprabhu. 2018. "High-Performance Platinum-Free Oxygen Reduction Reaction and Hydrogen Oxidation Reaction Catalyst in Polymer Electrolyte Membrane Fuel Cell." *Scientific Reports* 8 (1): 3591. https://doi.org/10.1038/s41598-018-22001-9.

Cheng, Chung-Fu, Han-Yu Hsueh, Chih-Huang Lai, Chun-Jern Pan, Bing-Joe Hwang, Chi-Chang Hu, and Rong-Ming Ho. 2015. "Nanoporous Gyroid Platinum with High Catalytic Activity from Block Copolymer Templates via Electroless Plating." *NPG Asia Materials* 7 (4): e170. https://doi.org/10.1038/am.2015.13.

Costamagna, Paola, and Supramaniam Srinivasan. 2001. "Quantum Jumps in the PEMFC Science and Technology from the 1960s to the Year 2000." *Journal of Power Sources* 102 (1–2): 253–69. https://doi.org/10.1016/S0378-7753(01)00807-2.

Debe, M. K. 2013. "Tutorial on the Fundamental Characteristics and Practical Properties of Nanostructured Thin Film (NSTF) Catalysts." *Journal of the Electrochemical Society* 160 (6): F522–34. https://doi.org/10.1149/2.049306jes.

Debe, M K. 2010. "Novel Catalysts, Catalysts Support and Catalysts Coated Membrane Methods." In *Handbook of Fuel Cells*. John Wiley & Sons, Ltd. https://doi.org/10.1002/9780470974001.f303050.

Debe, Mark K., Alison K. Schmoeckel, George D. Vernstrom, and Radoslav Atanasoski. 2006. "High Voltage Stability of Nanostructured Thin Film Catalysts for PEM Fuel Cells." *Journal of Power Sources* 161 (2): 1002–11. https://doi.org/10.1016/j.jpowsour.2006.05.033.

Debe, Mark K. 2012. "Electrocatalyst Approaches and Challenges for Automotive Fuel Cells." *Nature* 486 (7401): 43–51. https://doi.org/10.1038/nature11115.

Dhavale, Vishal M, and Sreekumar Kurungot. 2012. "Tuning the Performance of Low-Pt Polymer Electrolyte Membrane Fuel Cell Electrodes Derived from Fe_2O_3@Pt/C Core–Shell Catalyst Prepared by an in Situ Anchoring Strategy." *The Journal of Physical Chemistry C* 116 (13): 7318–26. https://doi.org/10.1021/jp300628j.

Ferreira, P. J., G. J. la O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, and H. A. Gasteiger. 2005. "Instability of Pt/C Electrocatalysts in Proton Exchange Membrane Fuel Cells." *Journal of The Electrochemical Society* 152 (11): A2256. https://doi.org/10.1149/1.2050347.

Gasteiger, Hubert A., Shyam S. Kocha, Bhaskar Sompalli, and Frederick T. Wagner. 2005. "Activity Benchmarks and Requirements for Pt, Pt-Alloy, and Non-Pt Oxygen Reduction Catalysts for PEMFCs." *Applied Catalysis B: Environmental* 56 (1–2): 9–35. https://doi.org/10.1016/j.apcatb.2004.06.021.

Ge, Xingbo, Xiuling Yan, Rongyue Wang, Fang Tian, and Yi Ding. 2009. "Tailoring the Structure and Property of Pt-Decorated Nanoporous Gold by Thermal Annealing." *The Journal of Physical Chemistry C* 113 (17): 7379–84. https://doi.org/10.1021/jp9008702.

Ghosh, A., S. Basu, and A. Verma. 2013. "Graphene and Functionalized Graphene Supported Platinum Catalyst for PEMFC." *Fuel Cells* 13 (3): 355–63. https://doi.org/10.1002/fuce.201300039.

Inaba, M., T. Suzuki, T. Hatanaka, and Y. Morimoto. 2015. "Fabrication and Cell Analysis of a Pt/SiO2 Platinum Thin Film Electrode." *Journal of the Electrochemical Society* 162 (7): F634–38. https://doi.org/10.1149/2.0201507jes.

Joghee, Prabhuram, Jennifer Nekuda Malik, Svitlana Pylypenko, and Ryan O'Hayre. 2015. "A Review on Direct Methanol Fuel Cells – In the Perspective of Energy and Sustainability." *MRS Energy & Sustainability* 2 (January): E3. http://journals.cambridge.org/abstract_S2329222915000045.

Karthikeyan, N., B. P. Vinayan, M. Rajesh, K. Balaji, A. K. Subramani, and S. Ramaprabhu. 2015. "Highly Durable Platinum Based Cathode Electrocatalysts for PEMFC Application Using Oxygen and Nitrogen Functional Groups Attached Nanocarbon Supports." *Fuel Cells* 15 (2): 278–87. https://doi.org/10.1002/fuce.201400134.

Kloke, Arne, Christian Köhler, Roland Zengerle, and Sven Kerzenmacher. 2012. "Porous Platinum Electrodes Fabricated by Cyclic Electrodeposition of PtCu Alloy: Application to Implantable Glucose Fuel Cells." *The Journal of Physical Chemistry C* 116 (37): 19689–98. https://doi.org/10.1021/jp306168t.

Kloke, Arne, Felix von Stetten, Roland Zengerle, and Sven Kerzenmacher. 2011. "Strategies for the Fabrication of Porous Platinum Electrodes." *Advanced Materials* 23 (43): 4976–5008. https://doi.org/10.1002/adma.201102182.

Li, Dongguo, Haifeng Lv, Yijin Kang, Nenad M. Markovic, and Vojislav R. Stamenkovic. 2016.

"Progress in the Development of Oxygen Reduction Reaction Catalysts for Low-Temperature Fuel Cells." *Annual Review of Chemical and Biomolecular Engineering* 7 (1): 509–32. https://doi.org/10.1146/annurev-chembioeng-080615-034526.

Liu, Pengpeng, Xingbo Ge, Rongyue Wang, Houyi Ma, and Yi Ding. 2009. "Facile Fabrication of Ultrathin Pt Overlayers onto Nanoporous Metal Membranes via Repeated Cu UPD and in Situ Redox Replacement Reaction." *Langmuir : The ACS Journal of Surfaces and Colloids* 25 (1): 561–67. https://doi.org/10.1021/la8027034.

Mahesh, Ijjada, and A. Sarkar. 2018. "Self-Restraining Electroless Deposition for Shell@Core Particles and Influence of Lattice Parameter on the ORR Activity of Pt(Shell)@Pd(Core)/C Electrocatalyst." *The Journal of Physical Chemistry C* 122 (17): 9283–91. https://doi.org/10.1021/acs.jpcc.7b12353.

McCurry, Daniel a, Martha Kamundi, Matthew Fayette, Fred Wafula, and Nikolay Dimitrov. 2011. "All Electrochemical Fabrication of a Platinized Nanoporous Au Thin-Film Catalyst." *ACS Appl. Mater. Interfaces* 3 (11): 4459–68. http://www.ncbi.nlm.nih.gov/pubmed/21981080.

Mohanraju, K., P.S. Kirankumar, L. Cindrella, and Oh. Joong Kwon. 2017. "Enhanced Electrocatalytic Activity of Pt Decorated Spinals (M3O4, M = Mn, Fe, Co)/C for Oxygen Reduction Reaction in PEM Fuel Cell and Their Evaluation by Hydrodynamic Techniques." *Journal of Electroanalytical Chemistry* 794 (June): 164–74. https://doi.org/10.1016/J.JELECHEM.2017.04.011.

Paddison, StephenJ., and HubertA. Gasteiger. 2013. "PEM Fuel Cells, Materials and Design Development Challenges." In *Fuel Cells SE - 11*, edited by Klaus-Dieter Kreuer, 341–67. Springer New York. https://doi.org/10.1007/978-1-4614-5785-5_11.

Puthusseri, Divya, and Sundara Ramaprabhu. 2016. "Oxygen Reduction Reaction Activity of Platinum Nanoparticles Decorated Nitrogen Doped Carbon in Proton Exchange Membrane Fuel Cell under Real Operating Conditions." *International Journal of Hydrogen Energy* 41 (30): 13163–70. https://doi.org/10.1016/J.IJHYDENE.2016.05.146.

Radhakrishnan, Thulasi, and N. Sandhyarani. 2019. "Pt-Ag Nanostructured 3D Architectures: A Tunable Catalyst for Methanol Oxidation Reaction." *Electrochimica Acta* 298 (March): 835–43. https://doi.org/10.1016/J.ELECTACTA.2018.12.151.

Sahoo, Madhumita, Keith Scott, and S. Ramaprabhu. 2015. "Platinum Decorated on Partially Exfoliated Multiwalled Carbon Nanotubes as High Performance Cathode Catalyst for PEMFC." *International Journal of Hydrogen Energy* 40 (30): 9435–43. https://doi.org/10.1016/j.ijhydene.2015.05.113.

Sha, Rinky, and Sushmee Badhulika. 2018. "Facile Synthesis of Three-Dimensional Platinum Nanoflowers on Reduced Graphene Oxide – Tin Oxide Composite: An Ultra-High Performance Catalyst for Methanol Electro-Oxidation." *Journal of Electroanalytical Chemistry* 820 (July): 9–17. https://doi.org/10.1016/J.JELECHEM.2018.04.057.

Solomon, Edward I., and Shannon S. Stahl. 2018. "Introduction: Oxygen Reduction and Activation in Catalysis." *Chemical Reviews* 118 (5): 2299–2301. https://doi.org/10.1021/acs.chemrev.8b00046.

Soren, S., B. D. Mohaptra, S. Mishra, A. K. Debnath, D. K. Aswal, K. S. K. Varadwaj, and P. Parhi. 2016. "Nano Ceria Supported Nitrogen Doped Graphene as a Highly Stable and Methanol

Tolerant Electrocatalyst for Oxygen Reduction." *RSC Advances* 6 (80): 77100–104. https://doi.org/10.1039/C6RA13218A.

Stamenkovic, Vojislav R., Dusan Strmcnik, Pietro P. Lopes, and Nenad M. Markovic. 2017. "Energy and Fuels from Electrochemical Interfaces." *Nature Materials* 16 (1): 57–69. https://doi.org/10.1038/nmat4738.

Sundarrajan, Subramanian, Suleyman I. Allakhverdiev, and Seeram Ramakrishna. 2012. "Progress and Perspectives in Micro Direct Methanol Fuel Cell." *International Journal of Hydrogen Energy* 37 (10): 8765–86. https://doi.org/10.1016/j.ijhydene.2011.12.017.

Tiwari, Jitendra N., Siraj Sultan, Chang Woo Myung, Taeseung Yoon, Nannan Li, Miran Ha, Ahmad M. Harzandi, et al. 2018. "Multicomponent Electrocatalyst with Ultralow Pt Loading and High Hydrogen Evolution Activity." *Nature Energy* 3 (9): 773–82. https://doi.org/10.1038/s41560-018-0209-x.

Vliet, Dennis F van der, Chao Wang, Dusan Tripkovic, Dusan Strmcnik, Xiao Feng Zhang, Mark K Debe, Radoslav T Atanasoski, Nenad M Markovic, and Vojislav R Stamenkovic. 2012. "Mesostructured Thin Films as Electrocatalysts with Tunable Composition and Surface Morphology." *Nature Materials* 11 (12): 1051–58. https://doi.org/10.1038/nmat3457.

Zeis, Roswitha, Anant Mathur, Greg Fritz, Joe Lee, and Jonah Erlebacher. 2007. "Platinum-Plated Nanoporous Gold: An Efficient, Low Pt Loading Electrocatalyst for PEM Fuel Cells." *Journal of Power Sources* 165 (1): 65–72. http://www.scopus.com/inward/record.url?eid=2-s2.0-33846874990&partnerID=40&md5=856ba7da9d59ea0f7cd7470ec4403cde.

4.0 Project Objectives:

- **Broad Objective**: Fabrication of conductive, electrocatalytically active, nanostructured films with Ultralow Platinum loading on Nafion membranes for PEMFC/DMFC applications

- **Specific objectives:**

  1) Use of pulsed electrodeposition technique to form 1-10 atomic layer thick platinum shells onto metallic nanostructured films.

  2) Electrochemical characterization of pulse-deposited Platinum films for benchmarking activity parameters for PEMFC/DMFC applications, such as ECSA values, Mass activity, CO tolerance, durability

5.0 Relevance of the work / Benefit to OECT/Country:

The ability to prepare ultra-low platinum loading electrodes for PEMFC/DMFC applications using an additive, roll-to-roll compatible process, will be a significant impetus for enabling widespread adaptation of fuel cells. Although, a few groups have reported the use of inkjet printers to fabricate MEAs using inks formulated from ionomer containing slurries of Pt/C particles, our proposed methodology will eliminate the need for colloidal ink formulation and can also enhance platinum utilization while lowering platinum loading by forming atomic overlayers onto inkjet printed conductive, nanoporous thin film substrates.

In the context of OECT, lowering the cost of PEMFC will enable the "Hydrogen" economy and provide a source for the utilization of natural gas. With Methanol being a lightweight energy carrier, DMFCs are actively pursued as an energy-efficient and quiet alternative to supply off-grid power for months – without any user intervention, e.g. for powering automatic control systems and fulfilling the electrical power demand for safety and security control aspects on off-shore oil rigs or other remote locations (https://www.efoy-pro.com/en/applications/oil-gas/).

6.0 Project need and Justification:

(Please also include definition of the problem)

The Oil and Gas industry faces a formidable task of meeting increasing energy demands while committing to significant reductions in gas emissions to combat global climate change. The most significant emitter of greenhouse gasses on offshore installations is gas turbines accounting for 81% of total greenhouse gas emissions. DMFCs are being considered as potential alternatives for such off-grid power supply applications. A recently undertaken SWOT analysis of fuel cell technology finds it competitive with gas turbines in terms of efficiency, emission, maintenance and downtime. But, significantly lagging in terms of cost [1].

Significant advances have been made in fuel cell system design over the last three decades concerning cost-reduction and structural design (see Section 3). But cost and durability problems associated with carbon support corrosion and loss of active surface area under PEMFC working

conditions, especially during start-up or shut down cycles have led to renewed interest in carbon-free nanostructured electrodes. In this context, there is scope for developing additive manufacturing processes, as well as novel electrocatalyst designs to further reduce platinum/PGM loading. *The goal of our research is to develop a cost-effective, additive process for manufacturing of membrane electrode assemblies with ultralow platinum loading for low-temperature fuel cells.*

The print-expose-develop technique developed in our group [2] has been used to fabricate porous, conducting silver nanostructures on Nafion membranes. We have been working on the idea of utilizing a self-terminating process for platinum monolayer deposition [3] onto inkjet-printed silver nanostructures to form conductive, porous, electrocatalytically active catalyst layers for PEMFC/DMFC applications. Our preliminary results confirm platinum deposition on metallic nanostructures with loading of <100 $\mu g_{Pt}/cm^2$, but optimization of process parameters is required to enhance electrocatalytic activity [4]. The ease of printing silver nanostructures using a simple inkjet printer and the ability to coat them with atomic-layers of platinum via cycling of electrode potential can pave the way for reducing the costs of PEMFC/DMFCs.

1. Nyberg, C.B., Master's Thesis, NTNU "Fuel Cells in Offshore Oil and Gas Production", 2017

2. Parmar et al. *Current Science* (2014): 262-269

3. Liu, Yihua, et al. *Science* 338.6112 (2012): 1327-1330.

4. Agrawal, K, Master's Thesis, IISc "Printed Electrodes for PEMFC". 2018

7.0 Methodology and Work Plan:

1. *Additive fabrication of catalyst layer*
   i. The print-expose-develop process developed in our group will be used to fabricate porous and conductive silver nanostructure films with particle or nanowire morphology on Nafion membrane.
   ii. We will use a self-terminating electrochemical deposition technique to fabricate platinum overlayers, in steps of monoatomic shells, on printed silver nanowire networks.
   iii. Electrochemical characterization of MOR/ORR activity will be carried out.

.

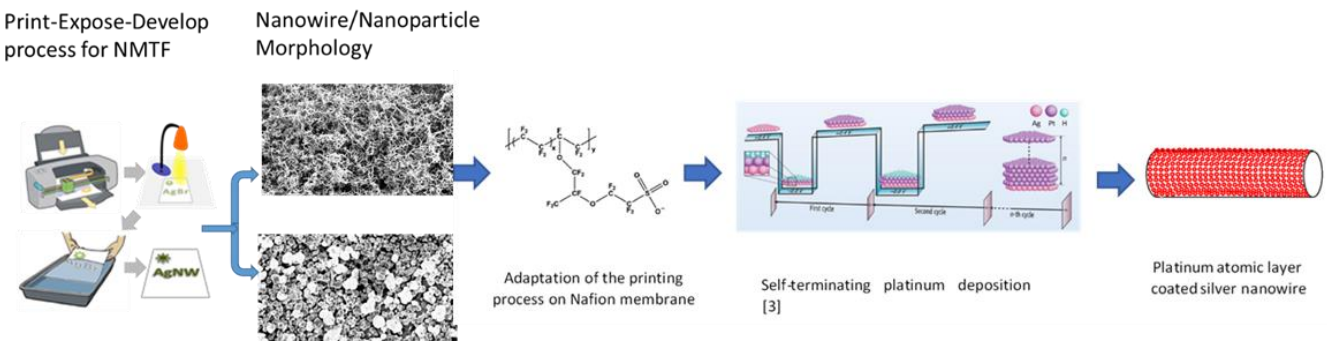


Fig.1 *Schematic illustrating the process flow for forming electrocatalyst layers.*

7.1 Time Schedule for Activities through Bar Chart:

Sl. No.	Major Activities	Time Period		
		(6 months)	(12 months)	(18 months)
1	**Proof of Concept** - Optimization of protocol for pulsed electrodeposition of platinum atomic layers			
2	**Procurement** of Rotating Ring Disk Electrode setup			
3	**Lab-Scale Demonstration** - Electrochemical characterization of MOR/ORR activity			

7.2 Milestones to monitor the Progress & Release of Installments:

No.	Milestones/Targets	Month from Start Date	Estimated Amount Requirement	Justification
i)	Initial release	**0**	**12 00 000**	Purchase of RDE setup, PMRF fellowship and consumables
ii)	Half-yearly Report, Procurement of RDE setup, **Proof of concept** Fabrication of Platinum coated conductive, electrocatalytically active nanostructures on Nafion membranes with **loading < 50** $\mu g/cm^2$	**6**	**5 00 000**	PMRF fellowship and consumables, travel contingency
iii)	Annual progress report, preliminary electrochemical characterization	**12**	**5 00 000**	PMRF fellowship, contingency and consumables Overheads for 1st year
iv)	**Lab-scale Demonstration** Optimization of number of platinum overlayers for enhanced electrocatalytic performance with **ECSA values > 80** m^2/g_{pt} and **Specific activity @0.9V of 0.44** A/mg_{pt} Submission of Final Technical Report and Audited Statements	**18**	**2 13 353**	Final settlement
	Total		**24 13 353**	

8.0 Potential Users, Market Assessment and suggested Plan of action for utilization of expected Project Output:

Alternative Energy and Automotive sectors will benefit from the development of low-cost printed electrocatalyst layers for fuel cells. The project output can seed the development of scaling-up strategies of the additive manufacturing process for fabricating low-cost fuel cell catalyst layers for pilot scale implementation and characterization of stability and durability. After pilot-scale study and technology optimization, field-trials can commence.

9.0 <u>Deliverables:</u>

9.1 Please specify the Project Specific Output:

- Additive fabrication process for carbon-support free nanostructured, electrocatalytically active and electrically-conductive thin film with ultralow platinum loading (< 50 $\mu g/cm^2$)
- Electrochemical characterization results for ORR/MOR activity and demonstration of optimal configuration(s) with ECSA > 80 m^2/g_{pt} and specific activity @0.9V >0.44 A/mg_{pt}

9.2 The other deliverables during / at the end of the project among other things will include:

a) Details of Research Papers/Technical Documents;

b) Project Reports (half-yearly);

c) IPR/Patents etc. including supply of samples of product/materials, essential for demonstration of process/protection of IPR or validation (For example: For biotechnology/microbiology project bacterial cultures, nutrient medium recipes, maintenance and deposition protocols for the isolates is required).

9.3 On completion of the project, other deliverables will include:

a) Final Project Report;

b) Detailed Documentation on proposed Technology/ Know-how on the Process/ Product and Safety Protocols (if applicable), which are prerequisite for further scaling up or pilot production;

c) Audited financial documents;

d) Audited list of assets.

SECTION - C

10.0 Budget

10.1 **Budget Estimates (Budget head wise break-up for the proposed project period)**

	Budget Head	First year	Second year	**Total**
	Capital Equipment	6 00 000	-	6 00 000
	Manpower*	5 15 712	2 57 856	7 73 568
	Consumable	4 00 000	2 00 000	6 00 000
	Travel**	25 000	25 000	50 000
	Contingency	50 000	25 000	75 000
	Any Other			
	Overheads @ 15%	2 38 607	76 178	3 14 785
	Total Estimated Budget	18 29 319	5 84 034	24 13 353

11.0 Justification for Budget (to be given for all the heads in Budget Estimates)

11.1 **Equipment:**

Sl. No.	Generic Name of the Equipment	Estimated Cost	Purpose
i.	**RDE (Rotating Disk Setup)**	6 00 000 (~9000 USD)	For characterizing the ORR/MOR specific activity of fabricated samples without diffusion limitations

11.2 **Manpower:**

Sl. No.	Designation	Yearly Rate	Duration in Months	Estimated Amount	Purpose
i.	PMRF fellow	5 15 712		7 73 568	OECT contribution towards PMRF fellowship for JRF

11.3 **Consumables:**

Sl. No.	Item	Quantities	Estimated Amount	Purpose
i.	Nafion membranes, Metal salt precursors etc		3 00 000	For preparing samples
ii.	CeNSE usage fees		3 00 000	Facility charges for materials characterization

SECTION – D

12.0 Details about the Institute/Organisation (Please also specify whether Central/ State/ Private / Autonomous):

IISc, Bangalore -- Autonomous Institute under MHRD

13.0 Infrastructural Facilities including capital equipment available with the Institute (relevant to the project work):

Fuel cell Test station, Material Characterization facility

14.0 Details of any MoU or NDC with any other Agency/ Institute/ Industry in the proposed and/or related field(s):

15.0 Biodata of Principal Investigator with details of previous experience of Project Proposer in proposed area of work, patents and publications etc., if any:

1. **Name and full correspondence address:** S. Venugopal (Venugopal Santhanam),
   Department of Chemical Engineering,
   Indian Institute of Science, Bangalore-560012.
   http://chemeng.iisc.ac.in/venu
2. **Email(s) and contact number(s):** svgpal@iisc.ac.in/venu.iisc@gmail.com
   Ph: 080 22933113, Mob: 9448833358, Fax: 080 2360812
3. **Institution:** Indian Institute of Science
4. **Date of Birth:** 25/03/1975
5. **Gender (M/F/T):** M
6. **Category Gen/SC/ST/OBC:** Gen
7. **Whether differently abled (Yes/No):** No
8. **Academic Qualification (Undergraduate Onwards)**

	Degree	Year	Subject	University/Institution
1.	B. Tech (Hons.)	1996	Chemical Engg	IIT Kharagpur
2.	M.S.	1998	Chemical Engg	Louisiana State Univ, Baton Rouge, USA
3.	PhD	2002	Chemical Engg	Purdue University, USA

9. **Ph.D thesis title, Guide's Name, Institute/Organization/University, Year of Award.**

Thesis: "Fabrication of nanoelectronic devices using self- assembled 2D arrays of monolayer protected clusters."
Advisor: Prof. Ronald P. Andres.
Purdue University, Dec 2002.

10. **Work experience (in chronological order).**

S.No.	Positions held	Name of the Institute	From	To
1	BAT-IIA Research Scientist	RWTH-Aachen	April 2003	Dec 2004
2	Assistant Professor	IISc, Bangalore	Dec 2004	Present

11. **Professional Recognition/ Award/ Prize/ Certificate, Fellowship received**

S.No	Name of Award	Awarding Agency	Year
1	Associate Member	Indian Academy of Sciences	2009
2	Humboldt Fellowship for Experienced Researchers	AvH foundation, Germany	2013

12. Publications relevant to proposal (Last 5 years)
Peer Reviewed Journals (Corresponding author/s underlined)

1. 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)
2. I. Banerjee, V. Kumaran, and V. Santhanam, "Fabrication of Electrodes with Ultralow Platinum Loading by RF Plasma Processing of Self-Assembled Arrays of Au@Pt Nanoparticles", *Nanotechnol.* 27, 305401 (2016)
3. I. Banerjee, V. Kumaran, and V. Santhanam, "Synthesis and Characterization of Au@Pt Nanoparticles with Ultrathin Platinum Overlayers", *J. Phys. Chem. C*. 119(11), 5982–5987 (2015)
4. S. Parmar, V. Santhanam, "*In situ* formation of silver nanowire networks on paper", *Curr. Sci.* 107(2)*, 262-269 (2014).*

Detail of patents.

S.No	Patent Title	Name of Applicant(s)	Patent No.	Award Date	Agency/Country	Status
1	Methods for preparing metal and metal oxide nanoparticles	**V. Santhanam**, S. K. Sivaraman	US 8361188	Jan 2013	**USPTO, USA**	**Owned by Intellectual Ventures**
2	Microelectronic component with electrically accessible metallic clusters	G. Schmid, U. Simon, D. Jaeger, **V. Santhanam**, T. Reuter	US 7602069; EP 1748501	Oct 2009	**USPTO, USA; EPO, Germany**	**Owned by Univ. of Duisburg-Essen**

Books/Reports/Chapters/General articles etc.

S.No	Title	Author's Name	Publisher	Year of Publication
1	"Scalable synthesis of noble metal nanoparticles" in Nanoscale and Microscale Phenomena , Eds. Y. Joshi, S. Khandekar,	**V. Santhanam**	Springer, India	2015
2	"Metal Nanoparticles: Self-assembly into Electronic Nanostructures", in The Dekker Encyclopedia of Nanoscience and Nanotechnology , 3rd edition, Eds. S.E. Lyshevski,	**V. Santhanam**, R.P. Andres	CRC Press, Taylir & Francis Group	2014

Any other Information (maximum 500 words)

The underlying theme of research activities in my group at IISc is the development of a process engineering 'toolkit' comprising of cost-effective and environmentally-benign processes that will enable the use of nanoparticles as building blocks in future nanoelectronic and energy conversion devices. We are also involved in the development of low-cost, additive fabrication techniques for forming nanostructured devices on flexible substrates.