NANO-CAT

Development of advanced catalysts for PEMFC automotive applications

Funding: European (7th RTD Framework Programme)
Duration: May 2013 - Jan 2017
Status: Complete with results
Total project cost: €4,394,331
EU contribution: €2,418,439

Objectives:

Many efforts have been put on the reduction of the Pt loading but nowadays a threshold seems to be obtained. Because the kinetics of the Hydrogen Oxidation Reaction is very fast on Pt, it is possible to use MEA with a Pt loading as low as 35 µgPt/cm-2 without any effect on the voltage loss when such an anode is used in front of a well working cathode. But, the Oxygen Reduction Reaction kinetics is not so fast which is the limiting step concerning the electrochemical processes in a PEMFC. For that raison, the decrease of the Pt loading is now encountering a plateau.

Nano-CAT will propose alternatives to the use of pure Pt as catalyst and promote Pt alloys or even Pt-free innovative catalyst structures with a good activity and enhanced lifetime due to a better resistance to degradation. Nano-CAT will thus develop novel Pt-free catalysts (called bioinspired catalysts) and explore the route of nanostructured Pt alloys with very low Pt content.

Catalysts are chemical species on which the electrochemical reactions are accelerated. PEMFC uses heterogeneous catalysis meaning the catalyst needs to be supported on a material in a solid phase (catalyst support). Nano-CAT will focus on the development of new supports with 2 promising sets of solutions: functionalized Carbon NanoTubes and conductive carbon-free Metal Oxide. These supports offering a better resistance towards degradation than the carbon black commonly used will address the issue of the support degradation and the MEA lifetime.

Nano-CAT will follow two routes, one low risk to ensure demonstration of the use of Pt alloys on new resistant supports and one high risk route to evaluate the feasibility of Pt-free MEA based on the use of bioinspired catalysts.

Finally, Nano-CAT addresses all technical issues leading to the industrialization of the project outcomes for automotive application by the development of high quality manufacturing methods of complete MEAs required to maintain high power density and efficiency.

Parent Programmes:
FP7-JTI - Specific Programme "Cooperation": Joint Technology Initiatives

Institute type: Public institution
Institute name: European Commission
Funding type: Public (EU)

Lead Organisation:

Commissariat A L Energie Atomique Et Aux Energies Alternatives

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75015 PARIS 15
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**Partner Organisations:**

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<td>C-Tech Innovation Limited</td>
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One of the major issue for PEMFC vehicles widespread is the cost of stack. In a study of 2012, for bus application, James showed that the stack cost represents 70% of the total system cost and 25% of the stack cost are due to the catalyst cost deposition process cost. And...

Executive Summary:

One of the major issue for PEMFC vehicles widespread is the cost of stack. In a study of 2012, for bus application, James showed that the stack cost represents 70% of the total system cost and 25% of the stack cost are due to the catalyst cost deposition process cost. And, the projections show that, by reaching a mass market and improving the number of stack released, the contribution of catalyst cost will become more and more important.

The amount of Pt in a Membrane Electrode Assembly (MEA) can be measured following different criterion, the Pt loading (g/cm²) which relates to mass of Pt per unit surface of MEA and Pt cost (g/kW) which relates to mass of Pt per unit of delivered electrical power. For the end users, the most important value is Pt cost because it will determine the part of the price of a system attributable to the catalyst. The Pt cost can be reduced either by increasing the power density (kW/cm² of MEA) of the cell for a given Pt loading (g/cm²) and/or by reducing the Pt loading for a given power density.

Nano-CAT proposes alternatives to the use of conventional catalyst and promotes nano-structured Pt based catalyst (or even Pt-free innovative catalyst structures) with a good activity and enhanced lifetime due to a better resistance to degradation. Nano-CAT will thus develop novel Pt-free catalysts (called bioinspired catalysts) and explore the route of nanostructured Pt and Pt alloys on innovative supports (carbon nanotubes and metal oxide). The project approach define in more detail here after is summarized by a chart presented in Figure 1.

Innovative support:

Catalysts are chemical species on which the electrochemical reactions are accelerated. PEMFC uses heterogeneous catalysis meaning the catalyst needs to be supported on a material in a solid phase (catalyst support). Nano-CAT will focus on the development of new supports with 2 promising sets of solutions: functionalized Carbon NanoTubes and conductive carbon-free Metal Oxide. These supports offering a better resistance towards degradation than the carbon black commonly used will address the
issue of the support degradation and the MEA lifetime.

Low Pt loading:

Nano-CAT will follow two routes, one low risk to ensure demonstration of the use structured Pt and Pt alloys on new resistant supports and one high risk route to evaluate the feasibility of Pt-free MEA based on the use of bioinspired catalysts. After validation of the activity of the developed catalyst using fine electrochemical technique, mainly Rotating Disk Electrode (RDE), the new catalyst are integrated in a MEA to be tested in single cell.

Finally, Nano-CAT addresses all technical issues leading to the industrialization of the project outcomes for automotive application by the development of high quality manufacturing methods of complete MEAs required to maintain high power density and efficiency.

Figure 1: chart of the project approach with high and low risk route

The material prepared and selected in the project are evaluated by performing accelerated test. A specific emphasis is put on the electrochemical characterisation of the active layer at begin and end of test. The protocol has been defined for bus application. That strategy allows the consortium to under more in detail the degradation mechanisms that occur under such condition, and then select resistant catalyst that are more stable under aggressive condition in order to slow down the degradation of performance and increase the life time of MEA.

Project Context and Objectives:

2.1 Project objectives

The main objective of the Nano-CAT project is to develop innovative catalyst structures and concepts with the potential of reaching long term cost and durability targets for PEMFCs in automotive applications.

Nano-CAT objective 1 will contribute to overcome the dependency on Pt as a catalyst and thus reduce the overall cost of the Watt produced.

1) Prove the concept of use of organic catalysts in MEA by providing an assembly containing no noble metal on both sides.

2) The current density under half cell configuration of the anodic bioinspired catalyst will reach hundreds mA/cm² which represents an increase of 2 orders of magnitude comparing to the actual state-of-the-art.

3) The current density under half cell configuration of the cathodic bioinspired catalyst will reach 100 mW/cm² which is the same order of magnitude as the one observe with Pt all along the pole curve.

Achievement: → The performance of the bio inspired material prepared in the project showed improvement toward the consortium SoA at the beginning of the project. The anodic material had an increase of performance of 1 order of magnitude in half cell and the cathodic material showed an overvoltage of 80 mV towards Pt/C 50% from TKK in RDE (acidic media). Nevertheless the hundreds of mW/cm² in half cell configuration has not been achieved.

Nano-CAT objective 2 will contribute to reduce the dependency on Pt with the use of Pt alloy as a catalyst and thus reduce the overall cost of the Watt produced.

1) Preparation of low Pt containing MEA. The Pt loading of the cathode will be reduced to lower than 0.1 mg/cm², which allows reaching 0.1 g/kW at maximum power density and at least 0.3 g/kW at 55% yield (676 mV).

2) A Power density of 1 W/cm² at 55% yield (0.676 V) will be reached with MEAs containing 0.3-0.5 mgPt/cm², which is twice less Pt than the state-of-the-art MEAs. 10 % loss will be accepted at the EoT (several hundreds of hours)

Achievement: → best developed MEA in the project reaches 1 W/cm² at 2 A/cm² (500 mV - 40 % yield). Anode loading was 0.1 mgPt/cm², cathode loading was 0.4 mgPt/cm². MEA has been aged under aggressive cycles representative of bus application. The loss of performance was 50 µV/h @ 475 mV during ageing test.

750 mW/cm² at 1.5 A/cm² has been achieved with 0.25 mgpt/cm² total which represents 0.3 gpt/kW max.

The conditions of the test was P: 1.5 bar, RH: 50% and T: 80°C. This could be modified according to the end user specifications.
Nano-CAT objective 3 will contribute to increase the lifetime of MEA.

1) Development of structured conductive MOx supports for catalysts suitable to be associated with Pt alloys at the cathode.

2) Development of CNTs and conductive MOx with which the loss of the ECSA at the cathode is below 50% (observed with carbon black), especially at middle temperature (100°C).

Achievement → structured conductive MOx supports has been prepared, Pt deposition has been made, the material performance has been assessed in RDE and MEA. Pt/SnO2-Sb showed lower degradation than ref commercial Pt/C material. Used of CNT as support for catalyst showed a lower degradation rate than commercial Pt/C catalyst both in RDE and single cell test.

Nano-CAT objective 4 will show that the new catalyst/support couples reach the specification given by the automotive end users, using harmonised testing procedures.

1) Development and validation of testing procedures insuring the improvement of the developments made within the project.

2) Accelerated tests for automotive application to measure the stack degradation.

3) Setup of a data base with results obtained with commercial and state-of-the-art catalysts to allow comparisons with Nano-CAT materials.

Achievement → Nano-CAT participate the networking group to establish EU harmonized procedure for the single cell test of MEA. The developed cycle in the project was aggressive and show specific mechanism to accelerate the anode degradation. The catalyst developed in NanoCAT as been evaluate against SoA commercial catalyst from TKK (Pt3Co/C, Pt/C and Pt/GC)

Nano-CAT objective 5 will contribute to ensure the manufacturability at low cost of the final product.

1) Different Catalyst deposition techniques will be developed for the new material and compared: PVD, wet chemistry, electro-deposition.

2) Technico-economic survey taking in account the raw material price and the process price will be done to show the advantages of the Nano-CAT materials.

3) The life cycle assessment of the Nano-CAT materials will be performed.

Achievement → Nano-CAT several routes for catalyst synthesis and AL preparation. The economic survey has been done using commercial BALLARD stack has reference (1W/cm2 @55% yield with 0.1 mgPt/cm2). The performance of the BALLARD stack could not be checked in the frame of the project and the conditions in which those performances are obtained were not checked.

Project Results:
Main outcomes of the project
Innovative catalyst support material.

The prepared metal oxide support (Sb doped SnO2,) allow to reach a conductivity of 1 S/cm which exceed by a factor 2.5 the target (0.4 S/cm). The xerogel process allow to reach a specific surface area of 85 m2/g..

picture of xerogel Sb doped SnO2 (10% at)

The preparation of N doped and N functionalised MWNTC as support to facilitate catalyst deposition has been performed. The synthesis by modification of industrial grade NTC has been updated to allow production of milligram batches, the chemical reaction is presented below. That progress allow to deliver high amount of material for catalyst deposition using wet chemistry process. Moreover highly purified MWNTC immobilized on GDL have been deliver for catalyst deposition suing PVD technique.

innovative route for preprartion of N-doped NTC.

Pt free material.
Many efforts have been put to increase current density using Pt free catalyst. For the first period, a special emphasis has been put on the ex situ characterization of the catalyst using RDE and half cell measurement techniques. Under half cell the Pt catalyst for HOR shows an increase of activity up to 40 mA/cm² @ 85°C (12 mA/cm² @ 25°C). Even if that result does not match the milestone MS 1 (100 mA/cm² @ 300 mV / Vs RHE), it is important to note that important progress has been made towards SoA. Indeed, in 18 months, the performance of the catalyst has been increase by a factor 10; the activity was only 3 mA/cm² @ 300 mV at the beginning of the project.

Regarding the development of Pt free catalyst for the ORR, an overvoltage of only 80 mV Vs Pt could be achieved. It was more than 130 mV at the beginning of the project. Moreover, in half cell measurement, that last catalyst generation gives an overvoltage of only 180 mV while 350 mV was observed with the previous one.

Deposition of catalyst of new and robust support.

A new route of catalyst deposition allowed us to develop a highly resistant catalyst toward corrosion. The performance of the catalyst has been validated thank to an ex situ measurement technique (Rotating Disk Electrode). The shape, dispersion and homogeneity of the catalyst has been validated by Scanning Electron Microscopy (SEM) and X-ray Diffraction (DRX).

First CNT and modified CNT has been prepared. The upscaling of highly purified CNT by thermal annealing has been validate and SEM images of the CNT are presented here below the CNT have a carbon purity equal to 99.9%. A new route to obtain N-doped CNT by plasma treatment under controlled atmosphere has been validated; that new routes allows to obtain atomic ration of N around 5% depending of the setup of the process.

SEM (left) and TEM (right) images of the CNTs collected from trial N°3

SEM images of different novel catalyst from the project (from left to right): Pt/CNT – Pt/ATO-EG and Pt/ATO-UV+H2

Among the different metal oxides evaluated as ORR catalyst support, Sb-doped tin dioxide (ATO) aerogel has been selected as the most promising one, with a relatively high specific surface area (85 m²/g), a multimodal pore size distribution (centerd on 20 and 45 nm) and an electronic conductivity of 0.12 S/cm.

Several catalysts were prepared on the new ATO aerogel support, following 3 different wet chemistry Pt deposition routes, all starting from H2PtCl6, 6 H2O as the platinum precursor. One was based on the use of ethyleneglycol as the reducing agent and stablizer of Pt nanoparticles (NPs). Pt NPs were first synthesized in solution and then deposited on the support after impregnation. In the two other routes, the support is first impregnated with the precursor solution which is then reduced by UV irradiation and/or hydrogen calcination, with or without pH control. Different Pt NPs size, cristallinity and repartition on the support surface were obtained, resulting in different electrocatalytic surface area (ECSA) and mass activity (MA) towards oxygen reduction. If the classical ethyleneglycol based route provided best performance, the UV irradiation combined with hydrogen calcination showed promising results.

Especially, ATO aerogels revealed to be highly resistant to corrosion at high potential, even in severe operating conditions (MEA AST cycling).

The deposition of catalyst nanoparticles has been optimised to functionalised highly purified CNT. The new preparation route allows to deposit highly and homogenously dispersed Pt nanoparticle (2.6 nm) on the CNT-HP surface.

MEA integrating catalyst on robust support.

A specific focus has been made to integrate the material in the MEA AL. To enhance the accessibility of reactant to the reactant, specific mixture of Pt/MWNCT and Pt/FGL has been developed. The added value of that material has been demonstrated in ex situ measurement (RDE). The stability of the Pt nanoparticles on CNT has been shown thanks to post-mortem nanocharacterisation.

SEM images of MEA cross section integrating commercial catalyst (TEC10V50E) from TKK (up and red) and Mix 4 catalyst from WP2 (down and green) after 30 kycycles of AST for catalyst dissolution, images of the catalyst (STEM modes) and size repartition of the catalyst nanoparticles

Improvement of MEA performance and durability including both NanoCAT catalyst and commercial
catalyst.

For the first period of the project, different MEA based on commercial catalyst has been tested. Test has been performed following specification given by Volvo. An emphasis has been put on the in situ and ex situ characterisation of the catalyst layer of the MEA. Thank to that willingness to understand degradation mechanism, we could propose new MEA with less degradation of performance while ageing using a protocol defined for bus application. The reference MEA and improved MEA (named A3199) have the same catalyst loading. The performances of both MEA are presented below. The performances of the improved MEA are 560 mW/cm² @ 55% yield and 750 mW/cm² @ 1.6 A/cm². The evolution of performance are shown below. The ageing tests have been performed using a segmented board in order to measure the local current density.

results of ageing test (AST) with reference MEA and improved MEA

In the second period, the prepared MEA in the project showed an improvement of performance toward begin of the project ref. 1 W/cm² has been reach and the degradation rate at 1.4 A/cm² under aggressive current cycle showed a low degradation rate of 50 µV/h only.

evolution of performance during ageing test of MEA integrating Pt/CNT-HP at the anode

Polcurve for MEA integrating Pt/NCT-HP at the anode at BoT and after ageing test (EoT)

Potential Impact:

Articles

Accepted:

- OZOUF, Guillaume, COGNARD, Gwenn, MAILLARD, Frédéric, GUETAZ, Laure, HEITZMANN, Marie, BEAUGER, Christian, Sn02 Aerogels: Towards Performant And Stable PEMFC Catalyst Supports, ECSTransaction 2015 69(17): 1207-1220
- COGNARD, Gwenn, OZOUF, Guillaume, BEAUGER, Christian, JIMENEZ-MORALES, Ignacio, CAVALIERE, Sara, JONES, Deborah, ROZIERE, Jacques, CHATENET, Marian, MAILLARD, Frédéric, Pt nanoparticles supported on highly porous niobium-doped tin dioxide: impact of the support morphology on Pt utilization and catalytic activity, Electrocataylsis, 8 (2017) 51, <10.1007/s12678-016-0340-z>.
in PEFCs operated with wet anode and dry cathode feed: A neutron imaging and modelling study, Journal of Power Sources, Status: submitted waiting the editor recommend for publication

Communications

- 226th ECS Meeting, October 5-9 Cancun (Mexico) Oral presentation “Effect of the Inlet Gas Humidification on PEMFC Behaviour and Current Density Distribution

  Authors: D. G. Sanchez, Tiziana Ruiu, Indro Biswas, K. Andreas Friedrich, Juan Sanchez-Monreal, Marcos Vera

- FCH review days (Bruxelles, November 11-12, 2014)

- FDFC 2015 (Toulouse, February 2015), Oral “Sb or Nb doped tin dioxide aerogels as catalyst support for PEMFC cathode”, G. Ozouf, C. Beauger.

- EERA Workshop (Roskilde, DTU, May 2015), Oral “Metal Oxides Aerogels as promising catalyst supports for Fuel Cells and Electrolysers“, C. Beauger


- ECS fall meeting (Phoenix, October 2015) Oral “Sn02 aerogels: towards performant and stable PEMFC catalyst support”, Guillaume Ozouf, Gwenn Cognard, Frédéric Maillard, Laure Guétaz, Marie Heitzmann, and Christian Beauger.


- 66th ISE Meeting, October Taipei (Taiwan) Comparison of the Degradation process during the bus application loading cycling in PEMFC. D. G. Sanchez, Indro Biswas, Denis Tremblay, P.A. Jacques, K. Andreas Friedrich ...

- 229th ECS Meeting, May29-june2 2016 San Diego 2

  Oral presentations:


  2° Water Distribution Oscillations in a PEMFC under Low Cathode Humidification: Neutron Imaging and Transient Two-Phase Modeling D.G. Sanchez, P. A. García-Salaberry, P. Boillat, M. Vera, K. Andreas Friedrich

- 1st workshop on rational design for improved functionalities of porous inorganic materials, Cavaillon, France, Nov 2016, BEAUGER, Christian, BERTHON-FABRY, Sandrine, RIGACCI, Arnaud, ACHARD, Patrick, Metal oxides aerogels for energy applications: fuel cells, water splitting


  Oral presentations:


ECS PRIIME 2016 Honolulu, 2-7 October 2016, OZOUF, Guillaume, COGNARD, Gwenn, MAILLARD, Frédéric, GUETAZ, Laure, HEITZMANN, Marie and BEAUGER, Christian, Sb or Nb doped tin dioxide aerogels based PEFC cathode

Materials Challenges for fuel cells and hydrogen, from innovation to industry, Sept 2016, Grenoble, France, BEAUGER, Christian, OZOUF, Guillaume, Metal Oxides Aerogels: catalyst support alternatives for Proton Exchange Membrane Fuel Cells,

ISASF 2016, Seminar on aerogels, Sophia-Antipolis, 22nd – 23rd September 2016 OZOUF, Guillaume, BEAUGER, Christian, Doped tin dioxide aerogel as alternative catalyst support for Proton Exchange Membrane Fuel Cells,


Oral presentation: D.G. Sanchez, P. A. García-Salaberri, P. Boillat, M. Vera, K. Andreas Friedrich. Neutron Imaging and Modelling of Autonomous Hydration-Dehydration Cycles in PEFCs Operated with Saturated Anode and Dry Cathode Feed

Workshop:

The 19-21 September 2016, the consortium organised a WS to disseminate the results from the project. 60 people attended to the WS. Internationally recognized scientific experts did oral presentation on their research in the field of material for PEMFC, characterization, stack testing and modelling.

Beyond the scientific presentation, the WS also hosted a specific session from the MATCH project. The goal was to identify the main scientific and technical bottlenecks to tackle in order to speed up the development of PEMFC. More information about MATCH could be find on the web site: http://www.match-a4m.eu/

List of Websites:
http://nanocat-project.eu/

Documents:
Final Report Summary - NANO-CAT (Development of advanced catalysts for PEMFC automotive applications)

STRIA Roadmaps: Vehicle design and manufacturing
Transport mode: Multimodal transport
Transport sectors: Passenger transport, Freight transport
Transport policies: Environmental/Emissions aspects, Other
Geo-spatial type: Other