CATAPULT

novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs

**Funding:** European (7th RTD Framework Programme)

**Duration:** Jun 2013 - May 2016

**Status:** Complete with results

**Total project cost:** €4,679,601

**EU contribution:** €2,255,690

**Objectives:**

Project CATAPULT proposes to develop a radically new concept for automotive PEM fuel cell catalysts based on novel structures wherein platinum is deposited as an extremely thin layer (<3 nm) on corrosion resistant supports of various morphologies, including particulate, nanofibrous and nanotubular, as well as "nano-hierarchical" combinations of these. In this approach, platinum is deposited using atomic layer deposition as thin, contiguous and conformal films that allow development of extended platinum or platinum alloy surfaces.

Non-PGM catalysts will be developed via the tailored synthesis of metal-organic frameworks for their use either sacrificially to generate the C/N support for non-PGM species, or directly as a non-PGM catalyst. Hybrid ultra-low Pt/non-PGM catalysts and catalyst layers will also be investigated as a further novel approach.

Increased fundamental understanding from supporting theoretical modelling will provide guidance to the strategies developed experimentally and to the down-selection of the new corrosion-resistant supports and their supported catalyst designs. Down-selected catalysts will be integrated into novel electrode designs and into MEAs incorporating state of the art membranes best adapted for automotive power trains, and evaluated according to protocols reproducing the stresses encountered in a drive cycle.

The candidate MEA best satisfying performance and stability targets will be scaled-up for further assessment at large MEA and short stack levels. Techno-economic assessment will consider the scale up processability, and the impact of MEA performance and durability on stack costs.

The well-balanced partnership, comprising two large industries (including an automotive OEM), two SMEs, two research organisations and two universities, will ensure close cooperation between industrial and institute partners, know-how, experience, research leadership, complementarity and industrial relevance.

**Parent Programmes:**

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

**Institute type:** Public institution

**Institute name:** European Commission

**Funding type:** Public (EU)

**Lead Organisation:**

Universite De Montpellier

**Address:**

163 RUE AUGUSTE BROUSSONNET
34090 MONTPELLIER
France
<table>
<thead>
<tr>
<th>Organisation</th>
<th>Website</th>
<th>EU Contribution</th>
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<td>Organisation Website:</td>
<td><a href="http://www.umontpellier.fr">http://www.umontpellier.fr</a></td>
<td>€302,778</td>
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### Partner Organisations:

#### Johnson Matthey Fuel Cells Limited

**Address:**
FARRINGDON STREET 25  
LONDON  
EC4A 4AB  
United Kingdom  

**Organisation Website:**
http://www.matthey.com  

**EU Contribution:** €450,891

#### Teknologian Tutkimuskeskus Vtt Oy

**Address:**
VUORIMIEHENTIE 3  
02150 Espoo  
Finland  

**Organisation Website:**
http://www.vtt.fi  

**EU Contribution:** €356,310

#### Universitaet Ulm

**Address:**
HELMHOLTZSTRASSE 16  
89081 ULM  
Germany  

**Organisation Website:**
http://www.uni-ulm.de  

**EU Contribution:** €159,366

#### Technische Universitaet Muenchen

**Address:**
Arcisstrasse 21  
80333 MUENCHEN  
Germany  

**Organisation Website:**
http://www.tu-muenchen.de  

**EU Contribution:** €308,546

#### Beneq Oy

**Address:**
OLARINLUOMA 9  
02200 ESPOO  
Finland  

**Organisation Website:**
Technologies:
- Fuel cells and hydrogen fuel
- Development of new Fuel Cells and Hydrogen (FCH) technologies

Key Results:

**Periodic Report Summary 2 - CATAPULT (novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs)**

Project Context and Objectives: Conventional platinum nanoparticles supported on high surface area carbon must be replaced at the fuel cell cathode by radically new materials types to produce the decisive step-change increase in mass activity to the target 0.44 A/mg Pt (at 900 mVIR-free). The CATAPULT project addressed these challenges by developing: i) ultra-low platinum loading MEAs using catalysts with ultra-thin extended film platinum coatings; ii) non-PGM based catalysts and hybrid ultra-low Pt/non-PGM catalysts and catalyst layers.

Developing a game-changing approach to fuel cell catalysts offered the opportunity of providing a solution to the problem of catalyst support degradation that severely limits fuel cell lifetime. The use of
fibrous structures as fuel cell catalyst supports is an emerging concept, which is particularly attractive from the point of view of their high surface area to volume ratio, as well as the void volume generated by their packing. Corrosion-resistant fibrous and tubular support structures were elaborated in CATAPULT by electrospinning, a versatile and up-scaleable approach allowing the fabrication of one dimensional mesostructured nanomaterials of controlled dimensions.

The CATAPULT project proposed to develop a radically new concept for PEM fuel cell catalysts wherein platinum is deposited as an extremely thin layer. In this approach, platinum is deposited as contiguous and conformal films, minimising sub-surface platinum and the contribution from edge and corner sites. As long as a sufficiently thin coating can be deposited, then it was considered possible to increase the platinum mass activity significantly beyond that which is possible with just further development of the current nano-particulate catalyst approach. In addition, considerable benefit with regard to durability was expected, since sintering is energetically unfavourable and the oxide-dissolution mechanism leading to Pt loss is significantly reduced. The extended platinum surfaces were elaborated using atomic layer deposition, allowing films to be built up monolayer by monolayer, on supports of any geometry. In an alternative approach, CATAPULT also aimed to investigate the electrochemical deposition of extended Pt and Pt alloy layers.

Increased fundamental understanding from theoretical modelling of the platinum surfaces most active for the oxygen reduction reaction and of the Pt-support binding energy, and how this depends on the number of Pt layers, as well as the impact of metal tie layers on lattice mis-match and binding energies, were designed to provide guidance to the strategies developed experimentally and to the down-selection of the new corrosion-resistant supports and their supported catalyst designs.

Our development of non-PGM catalysts was conceived so as to build on recent work highlighting the importance of the carbon/nitrogen support. In CATAPULT, tailored syntheses of metal-organic frameworks were planned to allow fine-tuning of the required properties for their use either sacrificially to generate the C/N support for non-PGM species, or directly as non-PGM catalysts. It was also intended to investigate the possible synergy of hybrid ultra-low Pt/non-PGM catalysts.

It was proposed to down-select catalysts for integration into novel electrode designs and into MEAs, and to evaluate MEAs according to protocols reproducing the stresses encountered in a drive cycle. CATAPULT targeted a catalyst mass activity of 0.44 A/mg Pt (at 900 mVIR-free) contributing to an MEA power density of ≥ 1.0 W/cm² at 0.67 V (1.5 A/cm², single cell) at beginning of life, and ≥ 0.9 W/cm² at 0.64 V (1.4 A/cm², single cell) at end of life. In the final part of the work, the aim was to scale-up the candidate MEA best satisfying performance and stability targets for further assessment. The results of the scale-up stage were designed as the key input to the techno-economic assessment, the output from which was to show whether the new catalyst concepts are compatible with the cost and durability targets.

Project Results:

The main results achieved in CATAPULT are listed below:

1. Corrosion resistant electronically conducting nanofibrous supports were prepared, the chemical composition of which was guided by modelling results generated in the first months of the project.

2. Oxide tie-layers were deposited on carbon nanofibre supports by atomic layer deposition. The corrosion resistance of the oxide-coated carbon support was increased dramatically, compared to un-coated carbon.

3. Pt was deposited by atomic layer deposition on fibrous supports. The mass activity of >0.5 A/mg Pt in RDE with these electrocatalysts exceeds the project target.

4. Innovative electrochemical methods of Pt deposition were successfully developed: over-potential deposition of thin Pt nano-islands on carbon nanofibres, microwave assisted galvanic displacement of nickel by Pt, and low temperature polyol deposition of Pt on Ni nanoparticles. The stability of the Pt on these supports in accelerated stress testing (voltage cycling) is greater than that of conventional Pt particles on conventional carbon.

5. The most mature catalyst was integrated into novel electrode designs, and the electrodes into MEAs of 50 cm² active area.

6. Performance testing was carried out on these MEAs, and accelerated stress testing in conditions relevant to automotive applications.

7. Methods for electrochemical and chemical characterisation of fibrous electrocatalysts were successfully developed, and greater knowledge and understanding of design rules for effective catalyst layer development with Pt layer/fibrous support electrocatalysts was generated.

8. A rational programme of development of non-PGM catalysts derived from metal organic frameworks
was implemented, and the structural properties of MOF components successfully related to the activity of the final catalyst.

9. A means of stabilising non-PGM catalysts to voltage decay during operation was discovered, based upon functionalisation with ultra-low amounts of Pt.

10. An internal technical assessment of results against conventional Pt nanoparticles on particulate C was carried out.

11. A voltage loss breakdown modelling tool was implemented to allow rational, objective assignment of voltage losses in MEAs.

12. A DFT-validated force-field model of the oxidative disruption of Pt crystal facets (111) was successfully developed, which showed that such facets would be unlikely to persist in real fuel cell operation.

13. Highly qualified personnel were trained, including BSc students (3), MSc students (3), PhD students (2) and post-docs (5), in addition to the training of two (6 months) student assistants.

14. A successful international conference was held 13-16 September 2016 on “Challenges for Zero Platinum for Oxygen Reduction”, which gathered 170 international specialists.

Potential Impact:

CATAPULT aimed at developing novel approaches to catalyst and catalyst layer design able to achieve low Pt usage requirement, whilst simultaneously addressing degradation issues associated with current catalyst support corrosion and Pt nanoparticle stability. Lowering Pt loading is the one remaining critical materials technology development required for the MEA, and the impact of being able to demonstrate this in project CATAPULT has a major impact on the prospects for widespread commercialisation of fuel cell powered vehicles. Nearly all vehicle OEMs subscribe to the need to attain such Pt loadings, whilst maintaining the high peak power densities, and also high electrical efficiency (cell voltages) at part-load, lower current density operation. Achievement of ca. 0.1 g/kW Pt equates to a requirement of ca.10 g Pt per vehicle (for a peak power requirement of 95 kW), and this is regarded as a key target by the automotive industry. As well as being compatible with the ultimate stack cost targets, it is also important to recognise that current gasoline and diesel powered internal combustion engines (ICEs) for medium to large size passenger cars require the use of precious metals for exhaust emission clean-up catalysts, the quantities of which when normalised to the price of Pt, equate to around 10 g Pt per vehicle. It has often been cited by the OEMs that they would like to employ no more precious metal content in FCVs than currently used in ICEs. In this scenario, platinum availability goes from being a reasonable constraint with the OEMs to being no constraint at all.

List of Websites:

http://www.catapult-fuelcells.eu/

Periodic Report Summary 1 - CATAPULT (novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs)

Project Context and Objectives:

Conventional platinum nanoparticles supported on high surface area carbon must be replaced at the fuel cell cathode by radically new materials types to produce the decisive step-change increase in mass activity to the target 0.44 A/mg Pt (at 900 mV IR-free). The CATAPULT project addresses these challenges by developing: i) ultra-low platinum loading MEAs using catalysts with ultra-thin extended film platinum coatings; ii) non-PGM based catalysts and hybrid ultra-low Pt/non-PGM catalysts and catalyst layers.

Developing a game-changing approach to fuel cell catalysts offers the opportunity of providing a solution to the problem of catalyst support degradation that severely limits fuel cell lifetime. The use of fibrous structures as fuel cell catalyst supports is an emerging concept, which is particularly attractive from the point of view of their high surface area to volume ratio, as well as the void volume generated by their packing. Corrosion-resistant fibrous and tubular support structures will be elaborated in CATAPULT by electrospinning, a versatile and up-scaleable approach allowing the fabrication of one dimensional mesostructured nanomaterials of controlled dimensions.

The CATAPULT project proposes to develop a radically new concept for PEM fuel cell catalysts wherein platinum is deposited as an extremely thin layer. In this approach, platinum is deposited as contiguous
and conformal films, minimising sub-surface platinum and the contribution from edge and corner sites. As long as a sufficiently thin coating can be deposited, then it will be possible to increase the platinum mass activity significantly beyond that which is possible with just further development of the current nano-particulate catalyst approach. In addition, considerable benefit with regard to durability is expected, since sintering is energetically unfavourable and the oxide-dissolution mechanism leading to Pt loss is significantly reduced. The extended platinum surfaces will be elaborated using atomic layer deposition, allowing films to be built up monolayer by monolayer, on supports of any geometry. In an alternative approach, we will also investigate the electrochemical deposition of extended Pt and Pt alloy layers.

Increased fundamental understanding from theoretical modelling of the platinum surfaces most active for the oxygen reduction reaction and of the Pt-support binding energy, and how this depends on the number of Pt layers, as well as the impact of metal tie layers on lattice mis-match and binding energies, will provide guidance to the strategies developed experimentally and to the down-selection of the new corrosion-resistant supports and their supported catalyst designs.

Our development of non-PGM catalysts will build on recent work highlighting the importance of the carbon/nitrogen support. In CATAPULT, tailored syntheses of metal-organic frameworks will allow fine-tuning of the required properties for their use either sacrificially to generate the C/N support for non-PGM species, or directly as non-PGM catalysts. The possible synergy of hybrid ultra-low Pt/non-PGM catalysts will also be investigated.

Down-selected catalysts will be integrated into novel electrode designs and into MEAs. They will be evaluated according to protocols reproducing the stresses encountered in a drive cycle. CATAPULT targets a catalyst mass activity of 0.44 A/mg Pt (at 900 mV IR-free) contributing to an MEA power density of ≥ 1.0 W/cm² at 0.67 V (1.5 A/cm², single cell) at beginning of life, and ≥ 0.9 W/cm² at 0.64 V (1.4 A/cm², single cell) at end of life. The candidate MEA best satisfying performance and stability targets will be scaled-up for further assessment. The results of the scale-up stage, and of the stack testing, will provide the key input to the techno-economic assessment, the output from which will be to show whether the new catalyst concepts are compatible with the cost and durability targets.

Project Results:

In the first eighteen months of CATAPULT, fifteen deliverable reports have been submitted and the two milestones of the period have been achieved. A low platinum loading catalyst sample with the innovative catalyst concepts of CATAPULT has shown very high mass activity, exceeding the final project target. Five non-platinum group metal catalysts have been prepared that show activity higher than that of the state of the art. A hybrid Fe-ultra-low Pt catalyst is showing high electrochemical stability. A brief outline of the achievements of the individual work packages is given below:

In WP2, the main result has been the specification of the performance and durability attributes of CATAPULT MEAs. Test protocols were exchanged to enable harmonisation at MEA and MEA component level. The purpose of these test protocols is to enable performance and robustness evaluation of MEAs as well as evaluate durability of the MEAs after having fulfilled performance targets.

Catalyst support structures with a range of compositions and low dimensional morphologies have been developed in WP3 using electrospinning, and the materials characterised for their corrosion resistance, electronic conductivity and structural and textural features. The target conductivity and electrochemical stability has been obtained with several oxide-type nanowire and nanotube materials and samples transferred to WP4 for platinum deposition.

In WP4, various approaches including atomic layer and electrochemical deposition have been investigated for platinum deposition on high surface area nanofibre supports. Investigation has been made of the various process conditions favouring formation of thin, continuous platinum films. Materials have been characterised using electron microscopy and electrochemical characterisation methods. An electrochemical method enabling determination of mass activity of fibrous catalysts has been developed. Two materials types show promise and ALD platinum on a nanofibre support and metal nanowires covered with platinum by a microwave-assisted galvanic displacement method. At least one of these catalyst materials exceeds the project final targets and is key output of this reporting period.

In WP5, three series of metal organic frameworks have been synthesised and evaluated for the synthesis of Fe-N-C catalysts obtained via the sacrificial MOF approach. Among those, five novel metal organic frameworks have resulted in Fe-N-C catalysts having an ORR activity at 0.9 V significantly higher than that reported for an optimised Fe-N-C catalyst derived from ZIF-8, which is the Fe-N-C catalyst with the highest initial ORR activity in PEMFC reported to date. The results obtained exceed the targets set at the project mid-term stage. Correlation has been made between key synthesis characteristics and high ORR activity after pyrolysis, which will be used to direct future work.

In WP6, based on former quantum-chemical calculations the oxygen adsorption as well as the ORR mechanism on Pt electrodes, a reactive force field (ReaxFF) for large-scale molecular-dynamics studies
has been developed and verified. Using this force field, various Pt/O/H systems suitable for the study of the ORR can be described reliably, while saving a considerable amount of computational time compared to DFT calculations. Promising non-carbon supports for platinum have been identified due to their binding and segregation properties by DFT calculations. In terms of activity and electrochemical cycling stability a candidate oxide-type support appears most suitable. These results provide input to WP3 for the preparation of future support materials.

In WP7, communication on the project has been achieved through early implementation of a project website and distribution of a project information leaflet, and dissemination has been made through ten presentations at international conferences. A conference on the Challenge of Zero Platinum for Oxygen Reduction is in an advanced stage of planning.

Potential Impact:

This project aims to develop such novel approaches to catalyst and catalyst layer design that can achieve such a low Pt usage requirement – whilst simultaneously addressing degradation issues associated with current catalyst support corrosion and Pt nanoparticle stability. Lowering Pt loading is the one remaining critical materials technology development required for the MEA, and the impact of being able to demonstrate this in project CATAPULT will have a major impact on the prospects for widespread commercialisation of fuel cell powered vehicles. Nearly all vehicle OEMs subscribe to the need to attain such Pt loadings, whilst maintaining the high peak power densities, and also high electrical efficiency (cell voltages) at part-load, lower current density operation. Achievement of ca. 0.1 g/kW Pt equates to a requirement of ca.10 g Pt per vehicle (for a peak power requirement of 95 kW), and this is regarded as a key target by the automotive industry. As well as being compatible with the ultimate stack cost targets, it is also important to recognise that current gasoline and diesel powered internal combustion engines (ICEs) for medium to large size passenger cars, such as the Euro 5 diesel car, require the use of precious metals for exhaust emission clean-up catalysts, the quantities of which when normalised to the price of Pt, equate to around 10 g Pt per vehicle. It has often been cited by the OEMs that they would like to employ no more precious metal content in FCVs than currently used in ICEs. In this scenario, platinum availability goes from being a reasonable constraint with the OEMs to being no constraint at all. This is an important impact for a successful project.

List of Websites:

http://www.catapult-fuelcells.eu/

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