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

CATAPULT (325268)

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

• Call topic AIP2012 Topic 1.5
• Application Area: Transportation & Refuelling Infrastructure
• Start date 1st June 2013; End date 31st May 2016
• Budget: total budget 4 678 599 €; FCH JU contribution 2 255 690 €; other external funding sources: TEKES funding 233 000 € to VTT

• Consortium overview

• To develop ultra-low Pt loading MEAs using ultra-thin extended film coatings on novel nanostructured supports, and non-PGM catalysts, with mass activity exceeding that of reference Pt/C with the aim of achieving a platinum specific power density of ≤ 0.1 g/kW Pt, providing ≥ 2 kW/l on representative power train profiles
• Report established at M24 (66% project duration passed)
## PROJECT TARGETS AND ACHIEVEMENTS

<table>
<thead>
<tr>
<th>Programme objective/target</th>
<th>Project objective/target</th>
<th>Project achievements to-date</th>
<th>Expected final achievement</th>
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<tr>
<td>RTD will mainly address ... inter alia: ... electrochemically stable and low-cost catalysts for MEAs ... Power density of ≥ 1.0 W/cm² at 0.67 V (1.5 A/cm², single cell) at BoL, and ≥ 0.9 W/cm² at 0.64 V (1.4 A/cm², single cell) at EoL, and providing platinum specific power density of ≤ 0.1 g Pt /kW</td>
<td>Development of electrochemically stable, novel ultra-low Pt loading MEAs using catalysts and electrodes using ultra-thin extended film Pt (alloy) coatings on novel nanostructured supports, non-PGM based catalysts and hybrid ultra-low Pt/non-PGM catalysts and catalyst layers. Same quantitative targets as MAIP</td>
<td>Development of novel ultra-low platinum loading catalysts using ultra-thin extended film platinum coatings on novel nanostructured supports, with high mass activity, initiation of electrode development with novel catalysts. Development of novel non-platinum group metal (PGM) based catalysts.</td>
<td>Power density of ≥ 1.0 W/cm² at 0.67 V (1.5 A/cm², single cell) at BoL, and ≥ 0.9 W/cm² at 0.64 V (1.4 A/cm², single cell) at EoL, and providing platinum specific power density of ≤ 0.1 g Pt /kW</td>
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**MAIP**
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<td>Development of robust and corrosion resistant supports</td>
<td>Nanometric supports with $\sigma &gt; 10^{-2}$ S/cm and 10x lower corrosion current over carbon black</td>
<td>Nanofibrous and nanotubular supports as self-supporting mats with $\sigma &gt; 10^{-1}$ S/cm and 10x lower corrosion current over carbon</td>
<td>Extend range of supports with requisite properties adapted for Pt deposition</td>
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<td>Development of catalysts and electrode layers allowing for significant reduction in precious metal loadings (ultra low loadings)</td>
<td>Development of catalysts by atomic layer deposition and electrochemical methods allowing mass activity &gt; Pt/C</td>
<td>Development of novel tie layers on fibrous supports and deposition of platinum by ALD and electrochemical methods, leading to thin extended platinum surfaces having mass activity &gt;0.5 A/mg Pt</td>
<td>Improved reproducibility</td>
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<td>Development of non-platinum based catalysts</td>
<td>Iron-based and hybrid non-PGM-ultra-low Pt loading catalysts High ORR activity allowing &gt;0.75 W/cm(^2) peak power and 500 h durability</td>
<td>Iron-based catalysts with high BoL performance, and stable hybrid non-PGM-ultra-low Pt loading catalysts.</td>
<td>&gt;0.75 W/cm(^2) peak power and 500 h durability</td>
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<td>Supporting theoretical modelling</td>
<td>Modelling for fundamental understanding of catalytic processes, support surfaces and catalyst-support interactions</td>
<td>DFT force field for study of ORR on Pt surfaces. Energetically favourable Pt-support tie-layers and Pt catalytic activity.</td>
<td>Improved understanding of voltage losses</td>
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<td>Long-term stability under automotive fuel cell conditions</td>
<td>Catalysts to be integrated into novel electrode designs and MEAs for evaluation using representative automotive power train load profiles.</td>
<td>Catalysts being prepared at larger scale and catalyst layer development is underway. Integration into a large single cell at M30.</td>
<td>Achieving target metrics</td>
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Selection of tie layers for Pt surfaces

- Pt-support interaction (binding energy) as a descriptor of the energetic likelihood of platinum wetting the support.
- Doping or reduction of oxides are favourable for wetting
- Wetting is more favourable on nitrides, carbides and metals
Corrosion resistant supports

- Nanofibrous or nanotubular supports using **electrospinning** - fibrous webs of doped oxides, carbides, carbon. For carbon fibres, combined with **atomic layer deposition** or **micro-wave deposition** to produce a protective oxide coating.

- Post-treatments as required, followed by Pt deposition.

Pt film on oxide or carbide support
Pt film on ceramic tie layer on carbon fibre

Ni nanoﬁbres
Fibre diameter ca. 250 nm

WC nanoﬁbres
Self-standing mat
Sheet σ ~20 S/cm

20 µm thick c-PAN
NbTiOx ALD on c-PAN

Ni ~ 150 nm

200 nm
Corrosion resistant supports

1.4 V/RHE, 80 degC, 0.5 M H$_2$SO$_4$ 2 h

- NbTiO$_x$ layer effectively protects against carbon corrosion
- Corrosion charge ($C_{mg^{-1}}$)
- C-PAN
- C-PAN + 25 ALD cycles NbTiO$_x$
- C-PAN + 50 ALD cycles NbTiO$_x$
- C-PAN + 100 ALD cycles NbTiO$_x$
- C-PAN + 200 ALD cycles NbTiO$_x$
- NbTiO$_x$

Electrospun PVA ALD with Ti-Nb-oxide
Annealing + removal of PVA leads to tubular structure

SbSnO$_x$ electrospun nanotubes and self-standing nanofibres for Pt ALD
• ALD NbTiOx on various supports, followed by ALD Pt.
• Conductivity of surface shows the connectivity of the platinum overlayer.
• Percolation occurs at >5 nm Pt on NbTiOx support for these systems.
• Recent developments have improved this to lower Pt thicknesses.
High mass activity Pt deposits

- Design capable of high Pt mass activity ($\approx 0.5 \text{ A/mgPt}$)
- Compromise between film and particle morphology
- Higher surface area than true film
- Higher stability than particles?
- Current focus is on reproducibility and MEA testing

Thin Pt islands formed by ALD on Nb-doped TiO$_x$, supported on carbonised PAN
Thin Pt film catalysts in MEAs

- CATAPULT MEA on SAE H₂/air polarisation test (80 °C 70% RH, 170 kPag)
  Pt loading = 0.13 mg/cm²
  Cathode catalyst is ALD Pt on conductive oxide coated carbon nanofibres.
  MEA created by spray-coating JMFC reinforced 17µm membrane with catalyst ink

No change in I-V curve after 30k cycles 0.6-1.0 volts
Modelling the ORR on a Pt surface

Microkinetic Modelling (composition 2 $\text{H}_2 : 1 \text{O}_2$)

Pt(111)  >  Pt(100)  >  Pt(110)
Non-noble metal catalysts

• Non-PGM catalysts derived from sacrificial Zn-based Metal Organic Frameworks

• Structure property correlation between cavity size (internal specific volume) of pristine MOFs and ORR activity of Fe-N-C catalysts - design tool for more active catalysts
Ultra-low Pt catalysts

- Similar initial ORR activity and fuel cell performance for H2-FeNC and Pt-FeNC catalysts
- FeNC and H2-FeNC unstable
- Pt-FeNC stable at Pt $\geq$ 1 wt %
- Hybrid Pt-FeNC catalyst with Fe-based ORR activity and Pt-like durability
- Apply approach to most active Fe-N-C catalysts i.e. with large cavity size
RISKS AND MITIGATION

Risk

• Translating high mass activity obtained in RDE testing with extended layer Pt catalysts on fibre supports to high mass activity in a fuel cell, due to the challenges of electrode development with completely novel catalyst structures

Mitigation

• Increase effort on electrode and MEA development

Risk

• Scaling up support, catalyst and electrode preparation in the project time-scale for short-stack characterisation

Remedial action

• Scale up support, catalyst and electrode preparation for large single cell characterisation
DISSEMINATION ACTIVITIES

  - 170 participants / 23 countries / 12 invited speakers / 30 contributed orals / 85 poster presentations / Proceedings publication planned in Int. J. Hydrogen Energy / Joint Session CATAPULT - CATHCAT - NanoCat - SmartCat

- Presentation of results at 8 other international conferences
- Two patents filed. Two publications to date.
HORIZONTAL ACTIVITIES

- Fuel Cells Short Course held prior to "Challenges Towards..." conference, La Grande Motte, on 13th September 2015. 40 international participants.

- Training within CATAPULT of:
  - 2 post-doctoral researchers in the synthesis and electrochemical characterisation of non-noble metal catalysts,
  - 1 PhD student and 1 post-doctoral researcher in electrochemical characterisation of extended Pt films on fibrous supports and on an electrochemical approach to deposition of Pt coatings,
  - 1 post-doctoral researcher in computational modelling of the oxygen reduction reaction on Pt surfaces,
  - 1 post-doctoral researcher on development and characterisation of corrosion resistant supports.
Synergies with CATHCAT, SMARTCAT and NANOCAT - joint session at the conference "Challenges towards zero Pt for oxygen reduction" (La Grande Motte, France, 13-16 Sept. 2015)

- PIs/participants of several DoE-funded low/zero Pt catalysts at "Challenges towards..." conference - numerous bilateral discussions
EXPLOITATION PLAN/EXPECTED IMPACT

• What has your project changed in the panorama of FCH technology development and/or commercialisation?
  – CATAPULT successfully confronts three areas in which materials improvements are required for automotive PEMFC: avoiding carbon corrosion, reducing Pt loading with extended layer ultra-low Pt and non-PGM catalysts.

• How will the project’s results be exploited? When? By whom?
  – Further RTD proposed for extended Pt layers and Pt thrifting approaches that have achieved TRL4 in CATAPULT, in FCH 2 JU proposal submitted 08/2015

• RTD projects:
  – What are the main results that go beyond international state-of-the art?
    • Catalyst mass activity for extended Pt layers on oxide supports
    • Activity and stabilisation of non-PGM catalysts
  – What are the achievements that will allow progressing one step further to cost reductions and enhanced performance (efficiency, durability)?
    • Reduced Pt loading (higher mass activity) Pt catalysts and hybrid ultra-low Pt/non-PGM catalysts for increased durability
  – How can the results from your project be taken on-board by industry?
    • Continued collaboration CNRS, VTT, JMFC (FCH 2 JU proposal O8/2015) for catalyst optimisation, up-scaling, catalyst layer and MEA development with CATAPULT catalysts