# 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

ATAPULT

- 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

TECHNISCHE UNIVERSITÄT MÜNCHEN cnrs Beneq VTT Johnson Matthey Fuel Cells the power within ulm university universität ulm PRETEXO

- 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

| Programme objective/target | Project objective/target | Project achievements to-date | Expected final achievement |
|---|---|---|---|
| **MAIP** | | | |
| 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/$cm^2$, single cell) at BoL, and ≥ 0.9 W/$cm^2$ at 0.64 V (1.4 A/cm2, single cell) at EoL, and providing platinum specific power density of ≤ 0.1 g Pt /kW | 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 | 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. | Power density of ≥ 1.0 W/cm2 at 0.67 V (1.5 A/$cm^2$, single cell) at BoL, and ≥ 0.9 W/$cm^2$ at 0.64 V (1.4 A/cm2, single cell) at EoL, and providing platinum specific power density of ≤ 0.1 g Pt /kW |

# PROJECT TARGETS AND ACHIEVEMENTS

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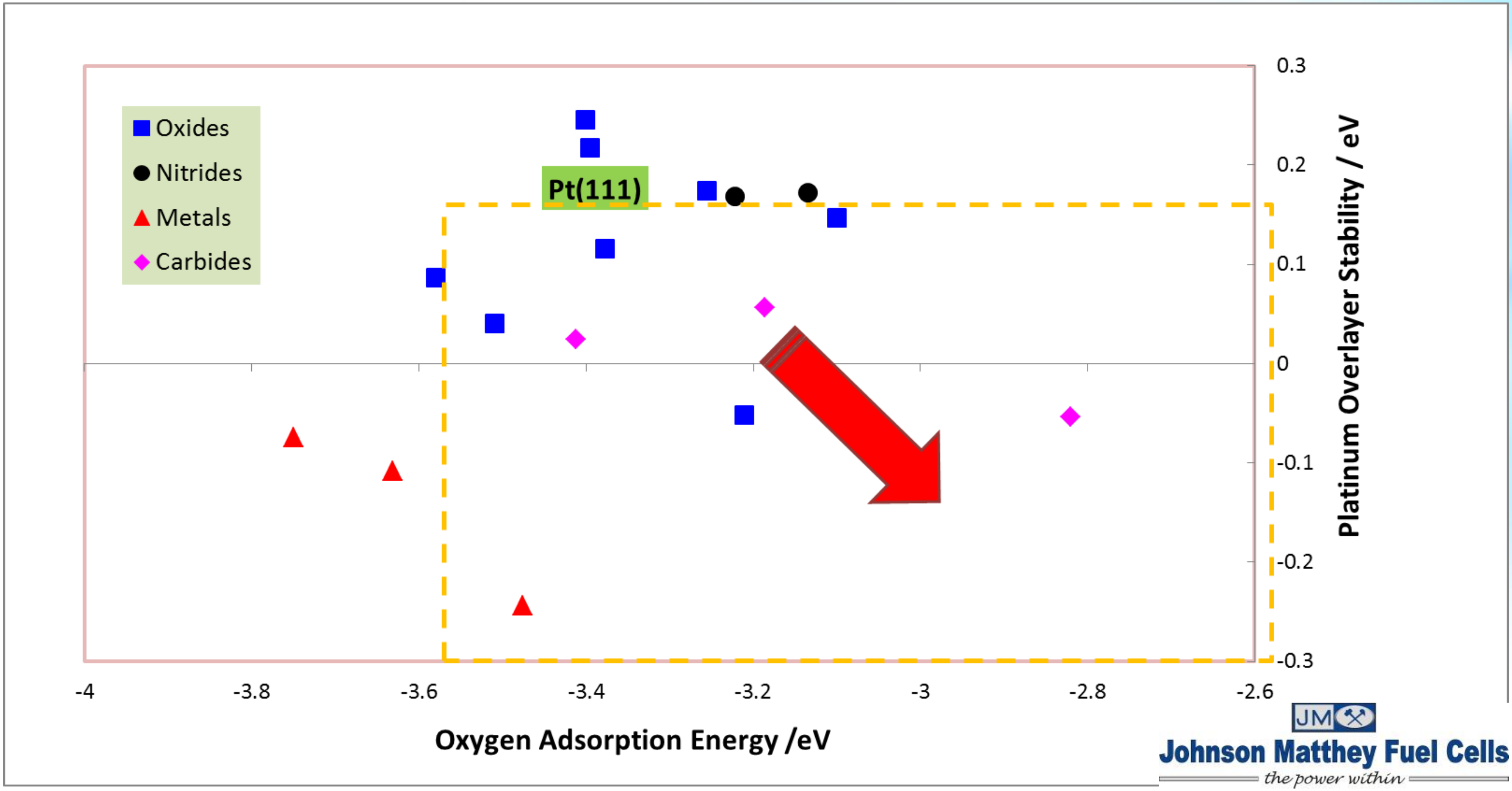
|---|---|---|---|
| **AIP** | | | |
| Development of robust and corrosion resistant supports | Nanometric supports with $\sigma > 10^{-2}$ S/cm and 10x lower corrosion current over carbon black | Nanofibrous and nanotubular supports as self-supporting mats with $\sigma > 10^{-1}$ S/cm and 10x lower corrosion current over carbon | Extend range of supports with requisite properties adapted for Pt deposition |
| Development of catalysts and electrode layers allowing for significant reduction in precious metal loadings (ultra low loadings) | Development of catalysts by atomic layer deposition and electrochemical methods allowing mass activity > Pt/C | 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 >0.5 A/mg Pt | Improved reproducibility |

# PROJECT TARGETS AND ACHIEVEMENTS

| Programme objective /target | Project objective/target | Project achievements to-date | Expected final achievement |
|---|---|---|---|
| **AIP** | | | |
| Development of non-platinum based catalysts | Iron-based and hybrid non-PGM-ultra-low Pt loading catalysts High ORR activity allowing >0.75 $W/cm^2$ peak power and 500 h durability | Iron-based catalysts with high BoL performance, and stable hybrid non-PGM-ultra-low Pt loading catalysts. | >0.75 $W/cm^2$ peak power and 500 h durability |
| Supporting theoretical modelling | Modelling for fundamental understanding of catalytic processes, support surfaces and catalyst-support interactions | DFT force field for study of ORR on Pt surfaces. Energetically favourable Pt-support tie-layers and Pt catalytic activity. | Improved understanding of voltage losses |
| Long-term stability under automotive fuel cell conditions | Catalysts to be integrated into novel electrode designs and MEAs for evaluation using representative automotive power train load profiles. | Catalysts being prepared at larger scale and catalyst layer development is underway. Integration into a large single cell at M30. | Achieving target metrics |

# Selection of tie layers for Pt surfaces

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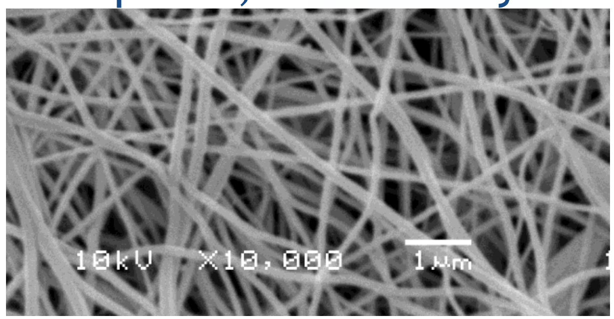
- Pt-support interaction (binding energy) as a descriptor of the energetic likelihood of platinum wetting the support.
- Doping or reduction of oxides are favourable for wetting
- Wetting is more favourable on nitrides, carbides and metals

# Corrosion resistant supports

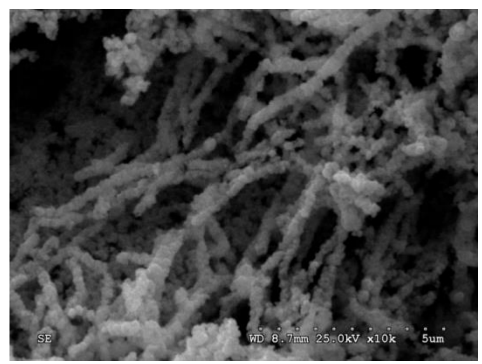
- Nanofibrous or nanotubular supports using **electrospinning** - fibrous webs of doped oxides, carbides, carbon. For carbon fibres, combined with **atomic layer deposition** or **micro-wave deposition** to produce a protective oxide coating
- Post-treatments as required, followed by Pt deposition



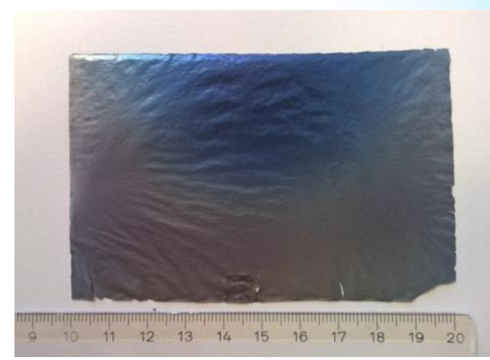


**Pt film on oxide or carbide support**

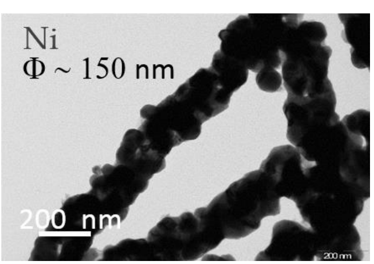
**Pt film on ceramic tie layer on carbon fibre**

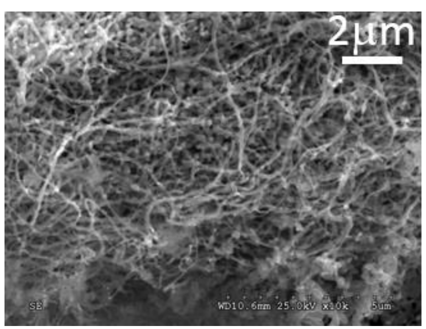


**NbTiOx ALD on c-PAN**



**sheet σ ~20 S/cm**



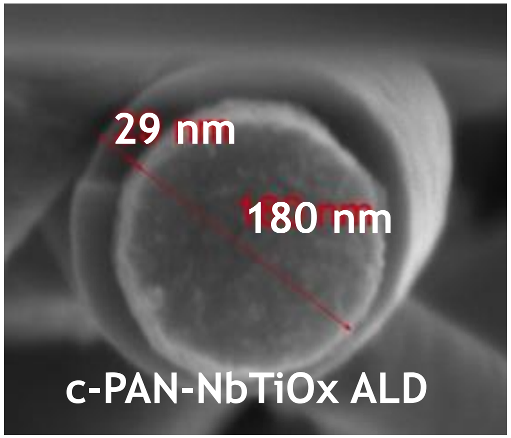



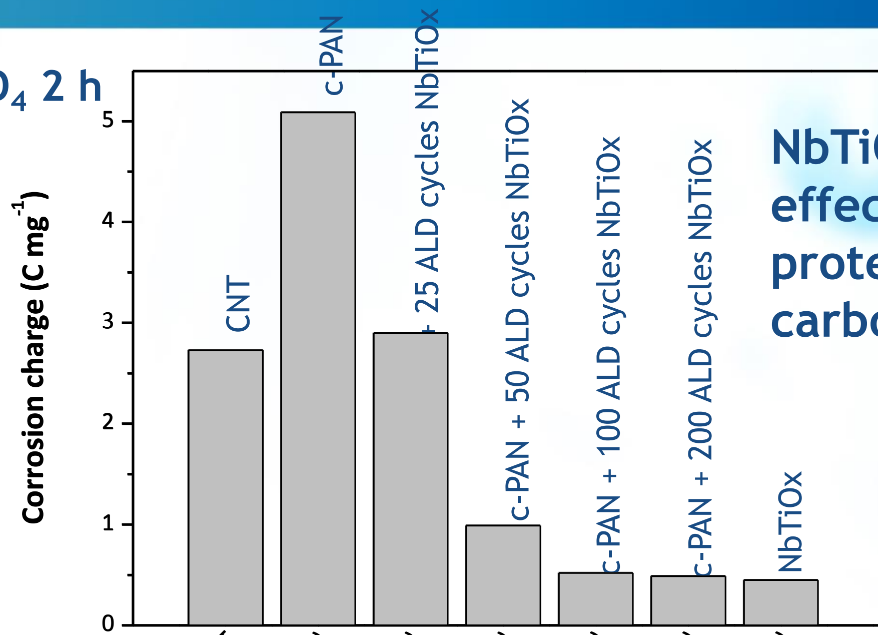

**Ni nanofibres**

**WC nanofibres**
**Self-standing mat**
**Fibre diameter ca. 250 nm**

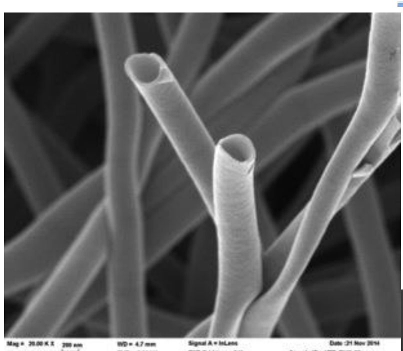
# Corrosion resistant supports

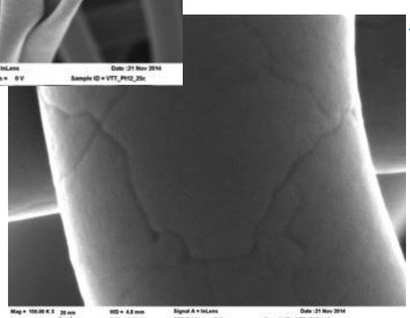
1.4 V/RHE, 80 degC, 0.5 M $H_2SO_4$ 2 h



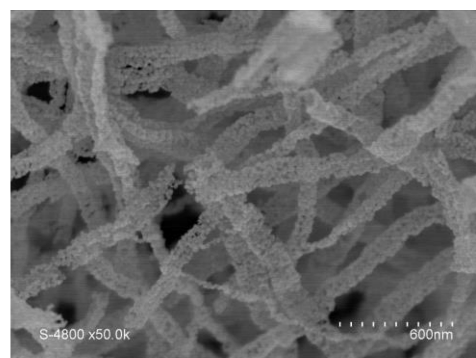

NbTiOx layer effectively protects against carbon corrosion

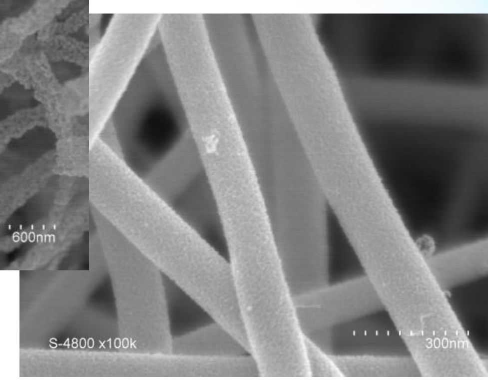




Electrospun PVA ALD with Ti-Nb-oxide

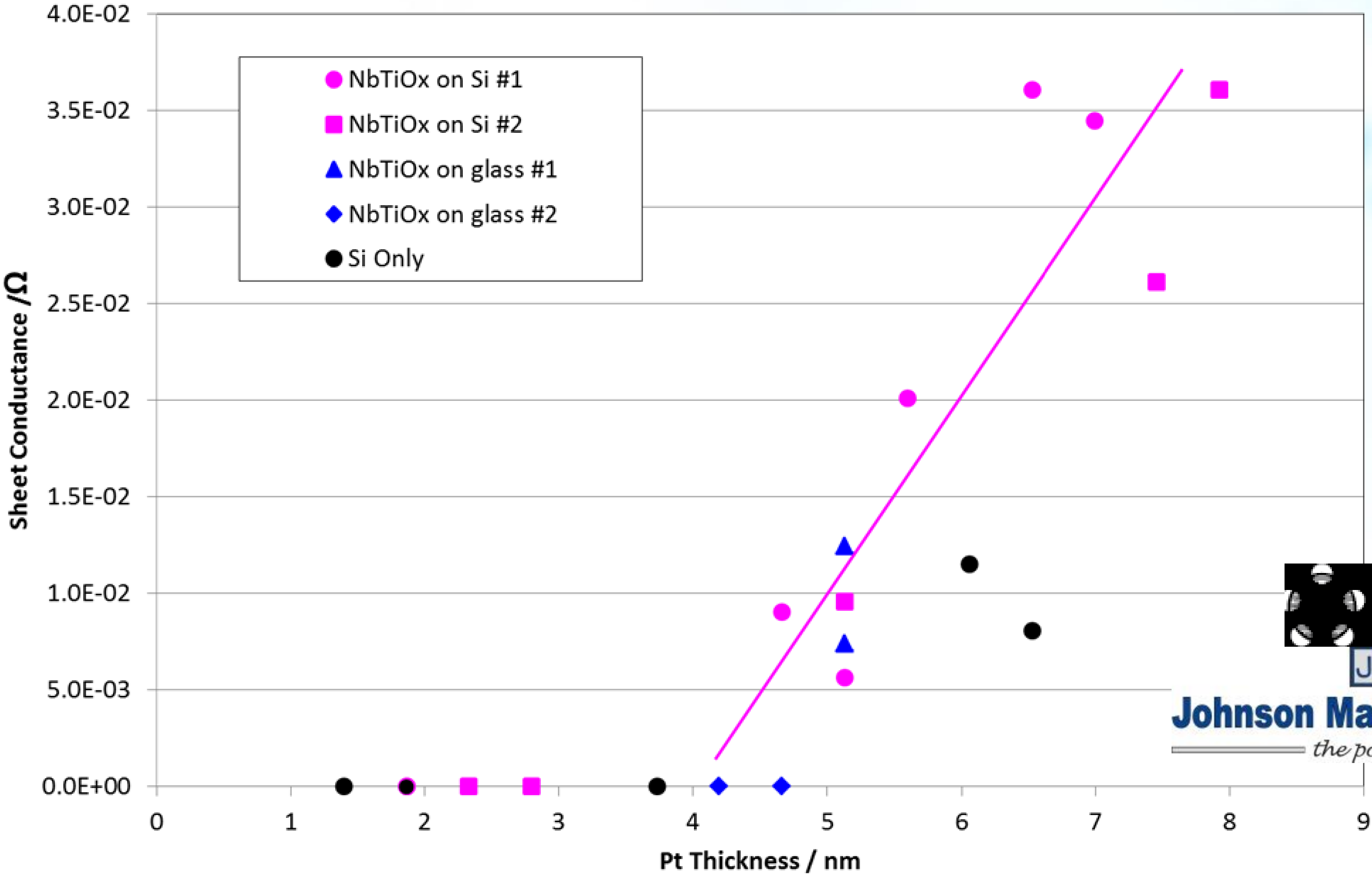
Annealing + removal of PVA leads to tubular structure



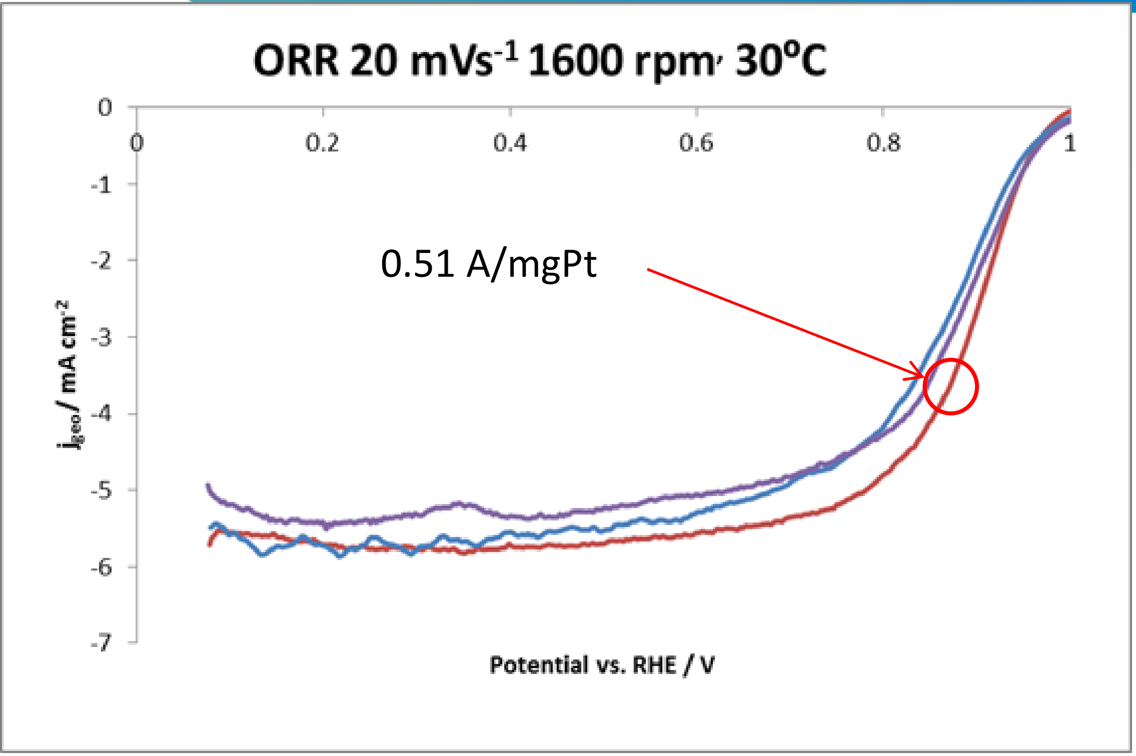

SbSnOx electrospun nanotubes and self-standing nanofibres for Pt ALD

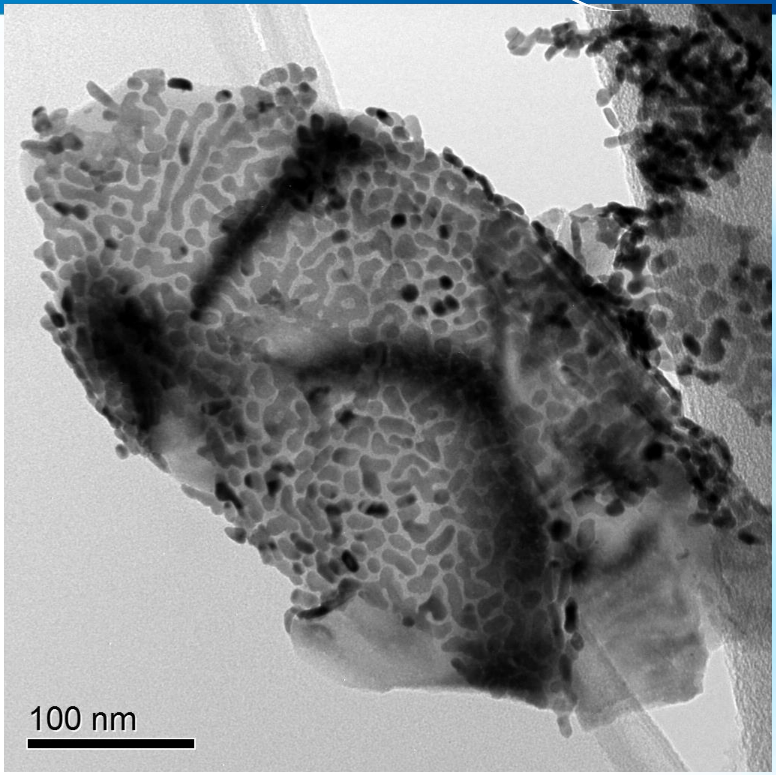
# Percolation threshold



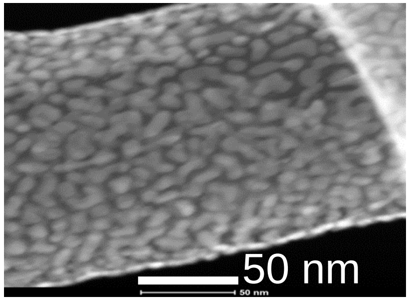

- ALD NbTiOx on various supports, followed by ALD Pt.
- Conductivity of surface shows the connectivity of the platinum overlayer.
- Percolation occurs at >5 nm Pt on NbTiOx support for these systems.
- Recent developments have improved this to lower Pt thicknesses.

# High mass activity Pt deposits




- Design capable of high Pt mass activity (≈0.5 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 TiOx, supported on carbonised PAN

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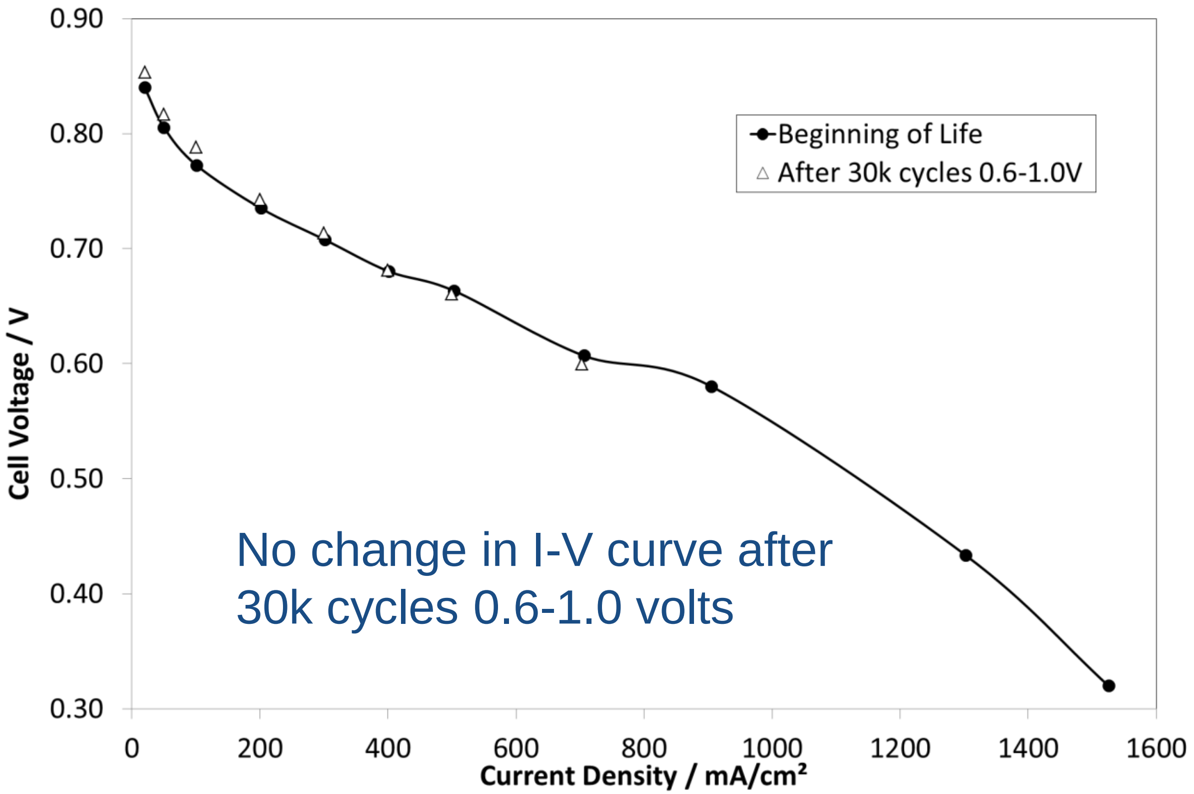
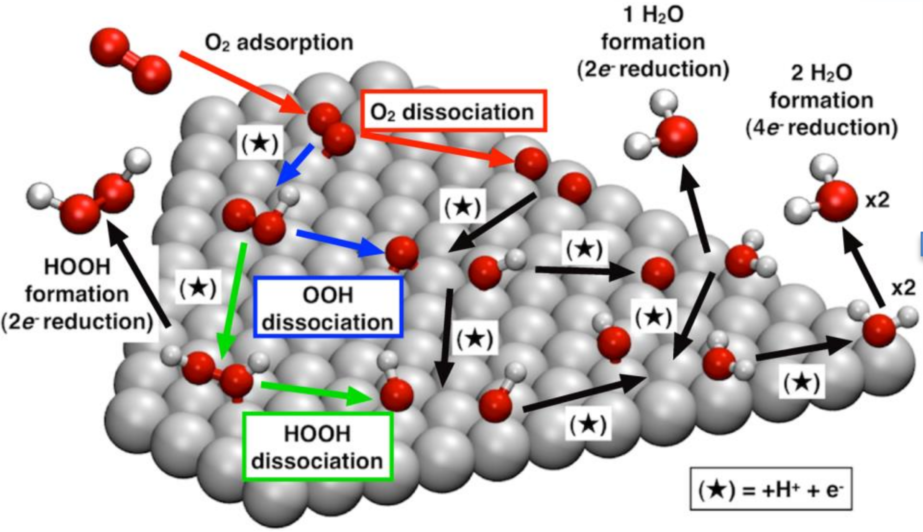
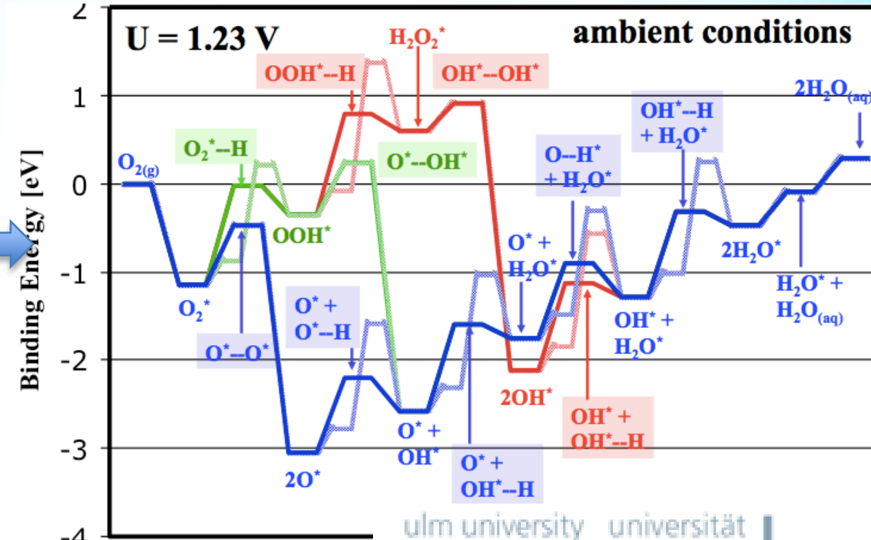
# Thin Pt film catalysts in MEAs

- CATAPULT MEA on SAE $H_2$/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



# Modelling the ORR on a Pt surface

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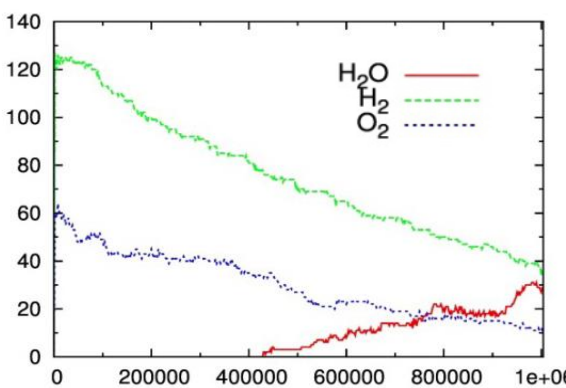
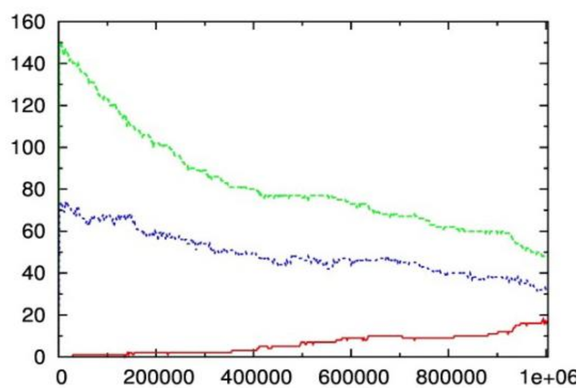
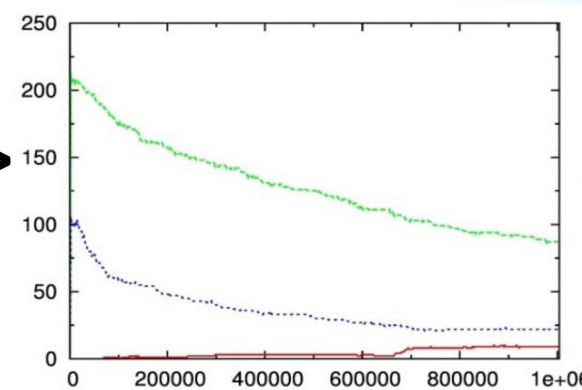
## Microkinetic Modelling (composition 2 $H_2$ : 1 $O_2$)

**Pt(111)** > **Pt(100)** > **Pt(110)**

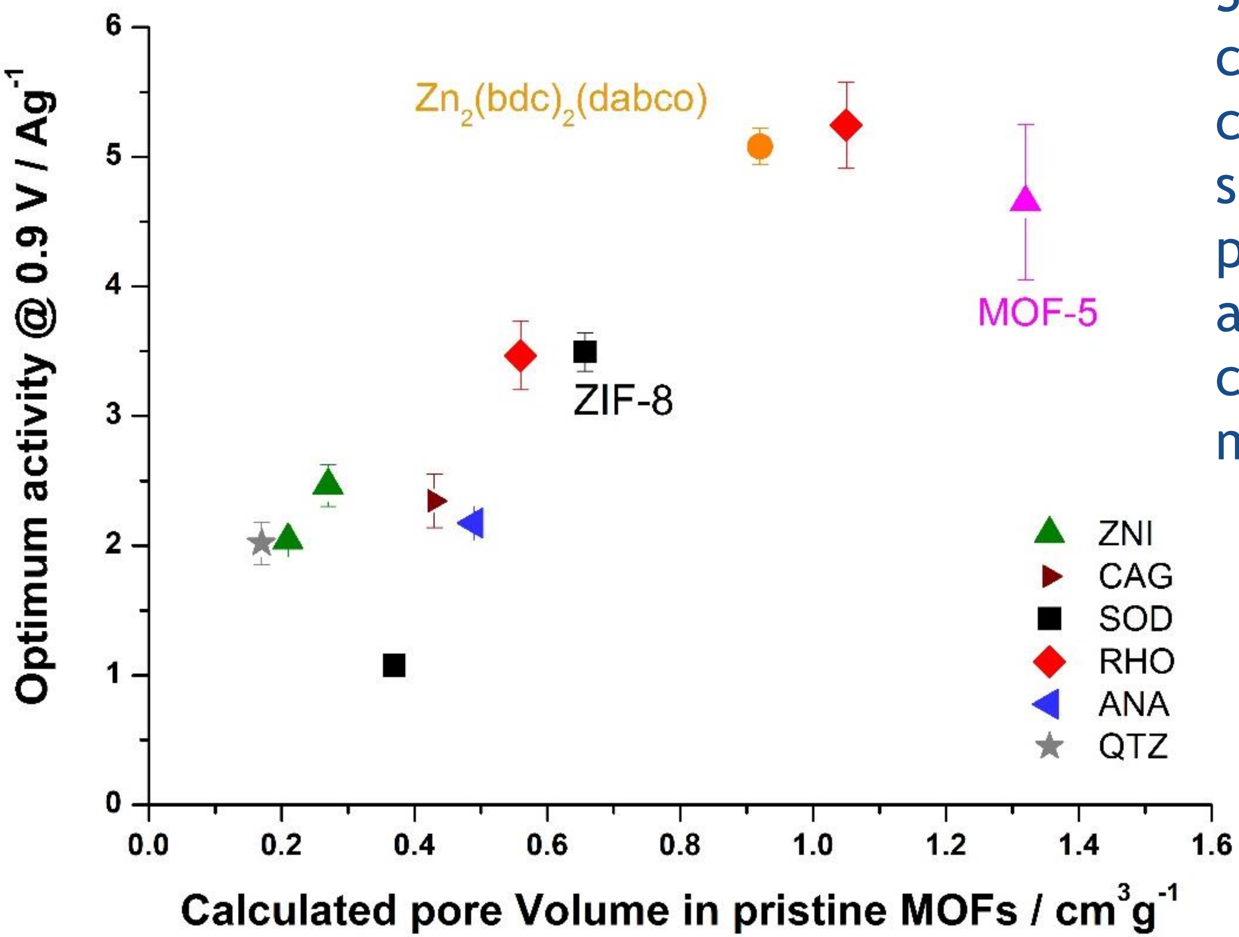




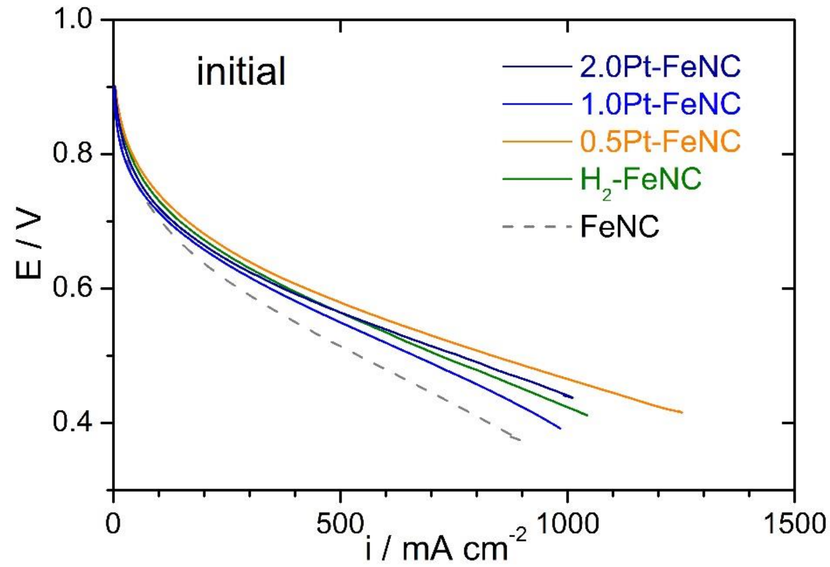
# Non-noble metal catalysts

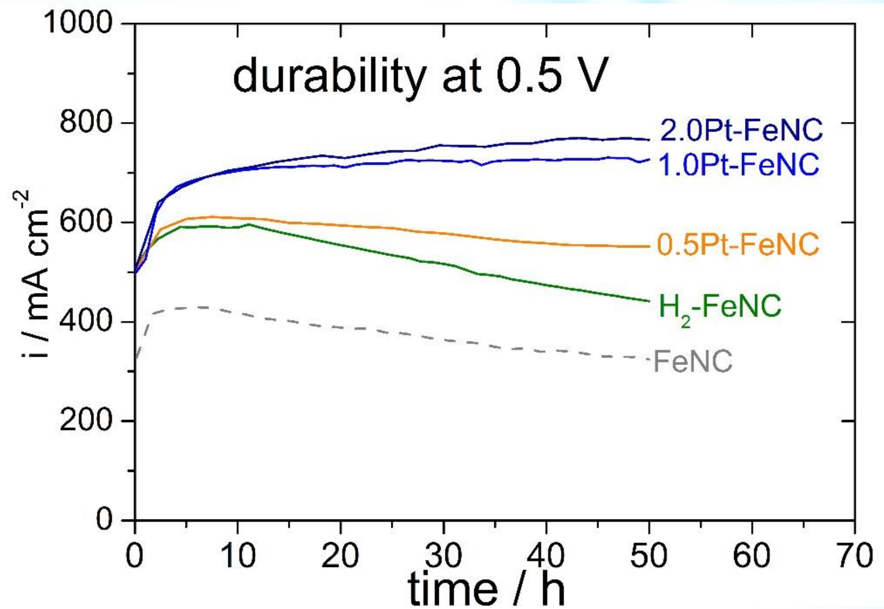
- Non-PGM catalysts derived from sacrificial Zn-based Metal Organic Frameworks




- 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 ≥ 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

- International conference organised by CATAPULT 13-16 September 2015 [http://www.efcd2015.eu/](http://www.efcd2015.eu/)


- 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 OTHER PROJECTS AND INITIATIVES

- 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 08/2015) for catalyst optimisation, up-scaling, catalyst layer and MEA development with CATAPULT catalysts