Publishable 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-strutured 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 unsig 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.

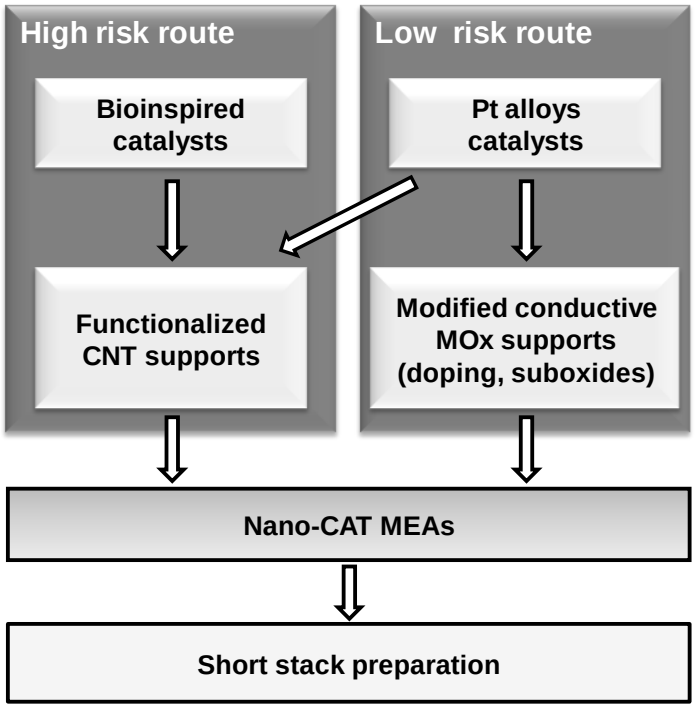


Figure 1: chart of the project approach with high and low risk route

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.

The project partners with their main activities are:

CEA: preparation of innovative catalyst and test in single cell, nanocharacterisation.

ARMINES: synthesis of conductive MOx for PEMFC application.

TECNALIA: preparation of innovative catalyst and test in single cell.

Nanocyl SA: preparation of improved NTC for PEMFC application.

JRC: test in stack.

C-Tech: technico-economic feasibility.

DLR: test in single cell and stack, electrochemical and naocharacterisation.

Volvo Technology AB: end user, protocol definition.

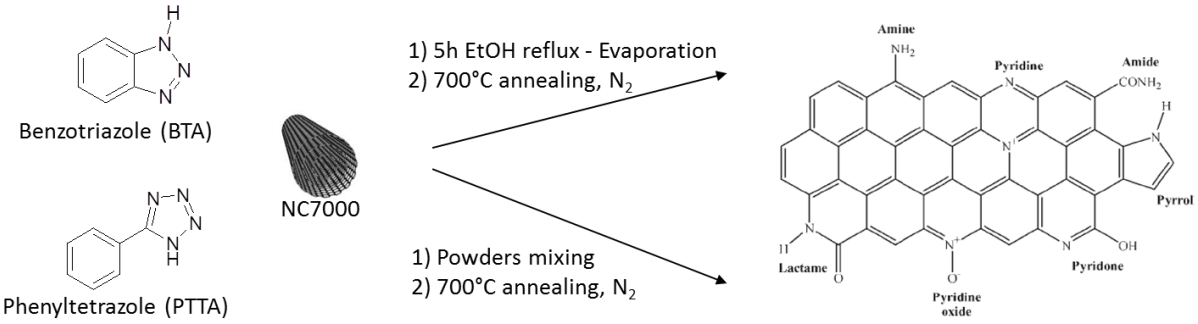
Main outcomes of the project

Innovative catalyst support material.

The prepared metal oxide support (Sb doped SnO_2, see **Erreur ! Source du renvoi introuvable.**) 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 m^2/g. **That progress allowed to reach the MS 6 and MS 8.**

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 in **Erreur ! Source du renvoi introuvable.**. 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. **That progress allowed to reach the MS 5**.



innovative route for preprartion of N-doped NTC.

Pt free material.

Many efforts has been put to increase current density using Pt free catalyst. For the first period, a special emphasis has been put on the ex situs 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/cm^2 @ 85°C (12 mA/cm^2 @ 25°C). Even if that result does not match the milestone MS 1 (100 mA/cm^2 @ 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/cm^2 @ 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 ().

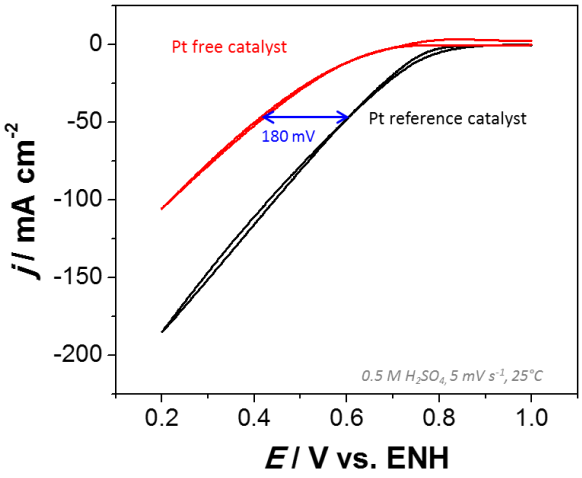


Figure 2: performance of ORR Pt free catalyst in half cell.

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.

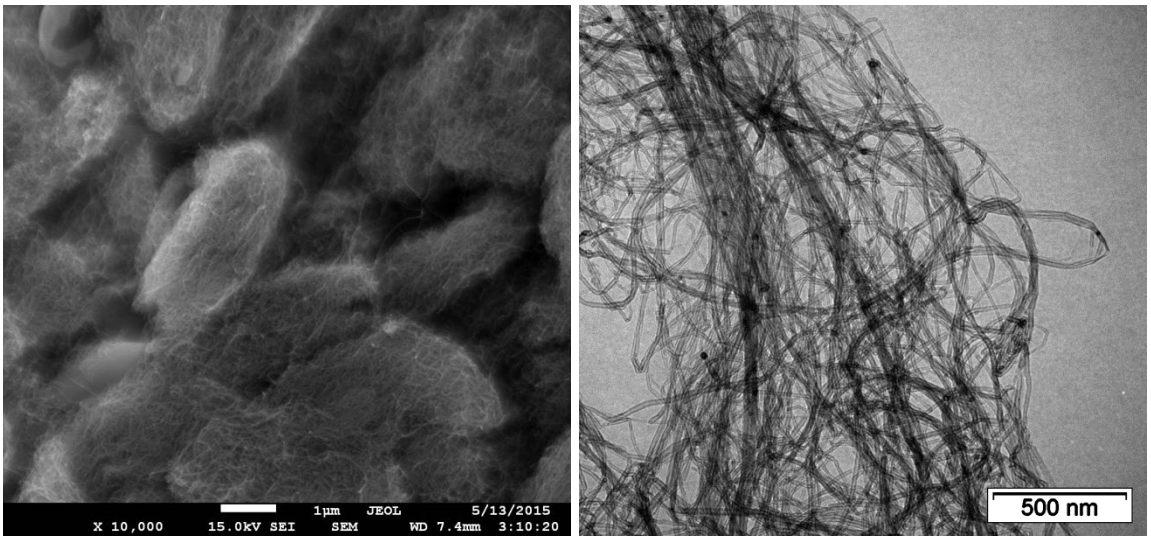


Figure 3: SEM (left) and TEM (right) images of the CNTs collected from trial N°3

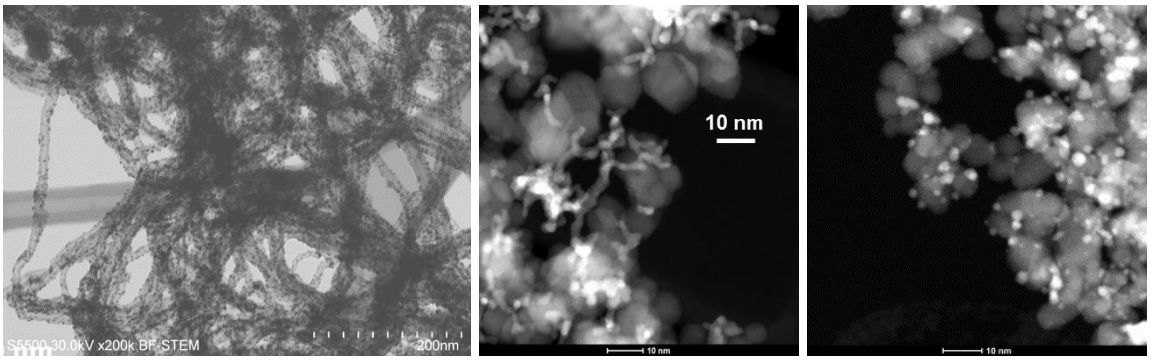


Figure 4: SEM images of different novel catalyst from the project (from left to right): Pt/CNT – Pt/ATO-EG and Pt/ATO-UV+H2

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 m^2/g), a multimodal pore size distribution (centerd on 20 and 45 nm) and an electronic conductivity of 0.12 S/cm.

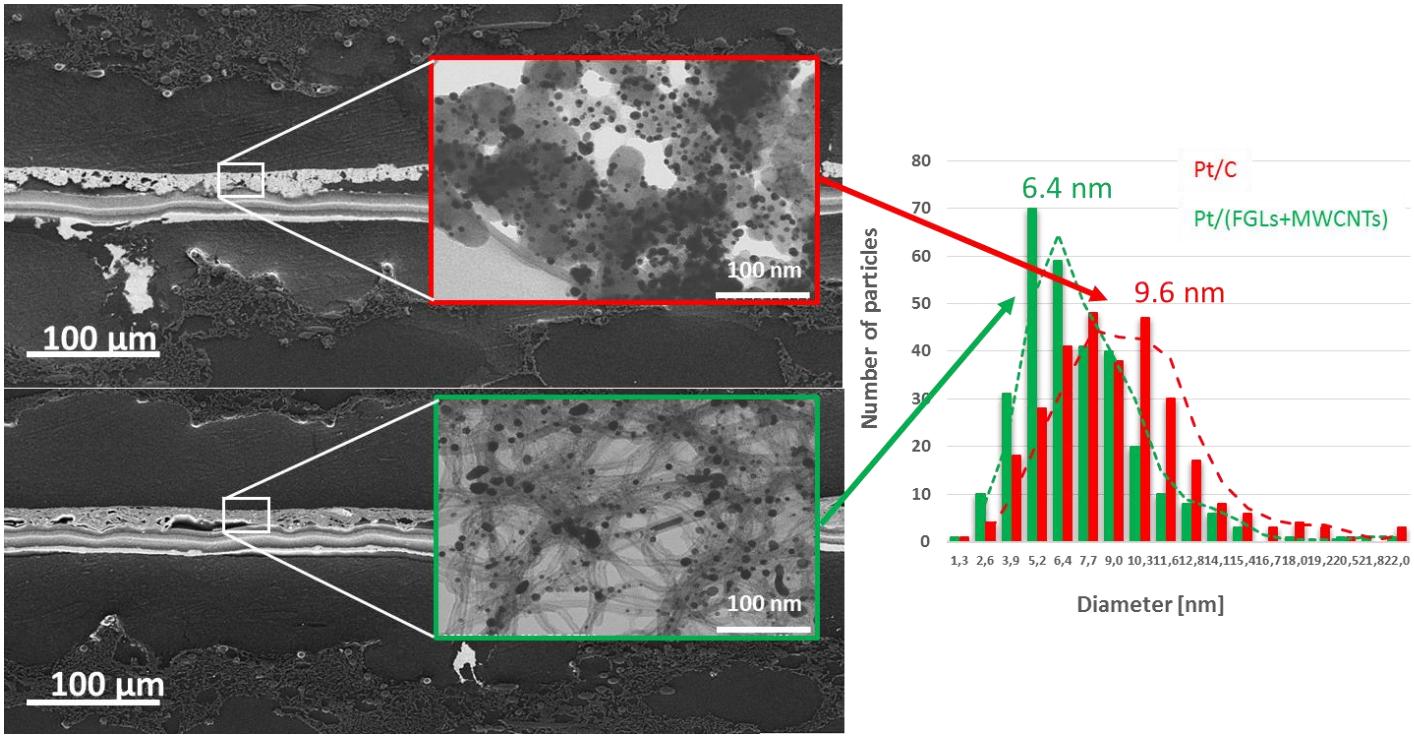
Several catalysts were prepared on the new ATO aerogel support, following 3 different wet chemistry Pt deposition routes, all starting from H_2PtCl_6, 6 H_2O as the platinum precursor. One was based on the use of ethyleneglycol as the reducing agent and stablizer of Pt nanoparticles

(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 ehtyleneglycol 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.

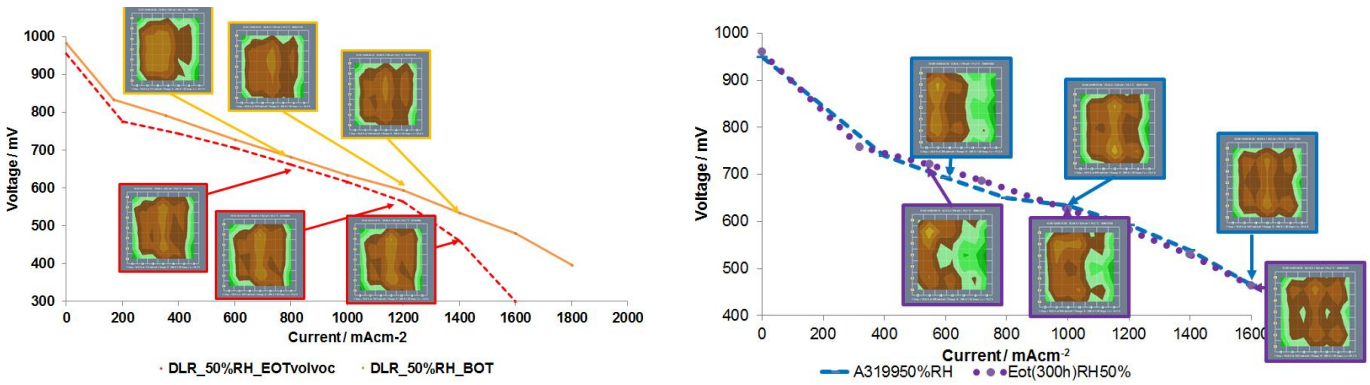
A specific focus has been made to integrate the material in the MEA AL. To enhance the accessibility of reactant to the reactant, specific mixture of Pt/MWNTC and Pt/FGL has been developed. The added value of that material has been demonstrated in ex situ measurement (RDE). The stability of the Pt nanoparticles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



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 kcycles of AST for catalyst dissolution, images of the catalyst (STEM modes) and size repartition of the catalyst nanoparticles

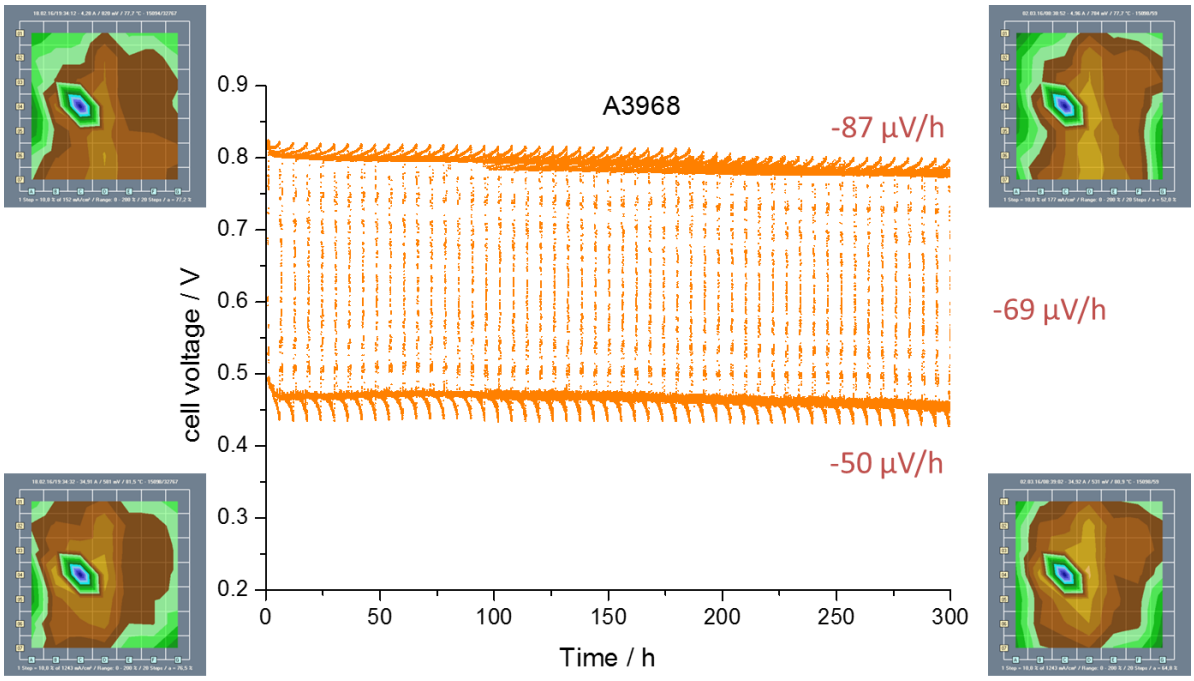
Improvement of MEA performance and durability including both NanoCAT catalyst and commercial catalyst.

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 situs and ex situs 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 performance 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 is shown **Erreur ! Source du renvoi introuvable.**. The ageing tests have been performed using a segmented board in order to measure the local current density.

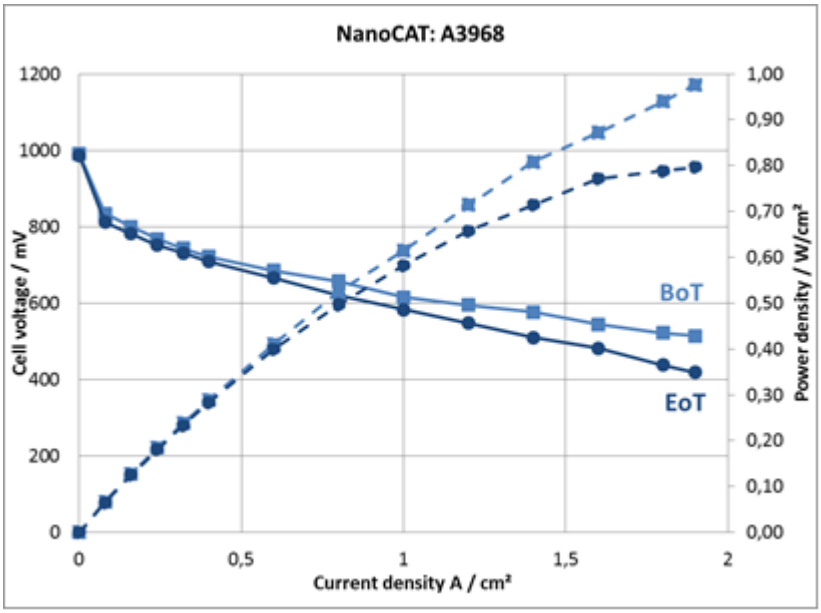


results of ageing test (AST) with reference MEA and improved MEA

In the second period, the prepared MEA in the project showed an improvement of performance toward begin of the project ref. 1 W/cm^2 has been reach and the degradation rate at 1.4 A/cm^2 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/CNT-HP at the anode at BoT and after ageing test (EoT)