INTEGRATION OF NOVEL STACK COMPONENTS FOR PERFORMANCE, IMPROVED DURABILITY AND LOWER COST

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# Deliverable Report

## Deliverable D3.2 – Catalyst Activity and Stability Studies

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## Nature of the Deliverable

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INSPIRE Deliverable Report D3.2 – Version 1 – 31/07/2017
SUMMARY

Keywords  Support, catalyst, mass activity, stability

Full Abstract (Confidential)  Pt, Pt alloy and ultra-low Pt materials have all been further advanced in the first 15 months. PtNi formulations as thin films (Task 3.3, CNRS), shaped particles (Task 3.4, TUB) and dealloyed catalysts (Task 3.4, JM) reach project mass activity and stability targets. The last of these was sufficiently prospective that the investigation of the feasibility of catalyst layers in fuel cell MEAs, to give high power density at high current density, was initiated earlier than planned, and validated at JM. Catalysts developed at TUB demonstrate extremely high initial mass activity of up to 3.4 A/mg Pt in RDE testing. For the longer term, high mass activity and high stability are expected from the complementary routes to Pt thin film deposition being developed on carbon fibre-carbon nanotube electrodes (Task 3.3, CNRS), transition metal doped carbons (Task 3.2, JM) and NbTiOx-tie layer protected carbon fibres and particles (Task 3.2 VTT and JM). Deposition of rare-earth metal-Pt alloys from ionic liquids is under development at TUM. In addition, the further optimisation of the composition and processing of ultra-low Pt Fe-NC hybrids (CNRS) will continue to extend the frontiers in the activity and stability of this class of catalysts.

Publishable Abstract (If different from above)

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CATALYST ACTIVITY AND STABILITY STUDIES

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1. Introduction

The key objective in WP3 is to advance catalysts of proven activity such that the performance (2.5 A/cm² at 0.6 V) and durability (6000 h) targets for project MEAs can be met. To meet these overall targets requires that the partners work towards a sub-set of objectives that comprise:

- Improved corrosion resistant catalyst supports, including corrosion-resistant carbons, oxides and carbides, as nanoparticles or nanofibres;
- Increase the stability of electrocatalysts of high surface specific activity and mass activity of at least 0.44 A/mg Pt;
- Demonstrate power density to within 10% of that of state of the art Pt/C at high (≥1.5 A/cm²) current density in small MEA testing, and high stability of power density in accelerated cyclic voltage testing;
- Scale-up one, or a maximum of two, of the best performing catalysts for transfer into WP4 for catalyst layer and CCM development in amounts needed to satisfy the requirements for stack MEAs.

Pt, Pt alloy and ultra-low Pt materials have all been further advanced in the first 15 months of INSPIRE and these developments are described below. The activities and stabilities of all catalysts are characterised using the same protocols agreed by the WP3 partners in the first months of INSPIRE, and applied by catalyst development partners JM, CNRS, TUB and TUM to a reference Pt/C and a baseline dealloyed PtNi/C catalyst provided by JM. The results of this benchmarking and calibration exercise are described in an earlier deliverable report, D3.1 “Report on activity and stability of reference catalyst”. In order to focus efforts only on the most prospective catalyst materials, “stage-gate” criteria have been defined that specify that initial and final (following accelerated ageing by voltage cycling) mass activities must exceed that of the reference Pt/C catalyst by a factor of two, whether determined by RDE or in a single cell fixture. By achieving these targets, the catalyst material is considered validated for progression into Task 3.6 to investigate the feasibility of catalyst layer development and thereafter, if that feasibility is demonstrated, of catalyst scale-up.

Four types of catalyst development were included in the Milestone 1 report, by having shown “Progress towards final WP3 targets of mass activity in MEA test, stability via agreed accelerated stress test (AST), and high current density performance (1.5 A/cm²) within 10% of that provided by the reference Pt/C”.

The current status is that PtNi formulations as thin films (Task 3.3, CNRS), shaped particles (Task 3.4, TUB) and dealloyed catalysts (Task 3.4, JM) reach the project mass activity and stability targets. In fact, the last of these demonstrated sufficient promise to warrant starting Task 3.6 earlier than planned, which puts WP3 in a good position with respect to reaching the mid-term deliverable of a scaled-up catalyst for validation in the GEN 2 stack design. Catalysts from TUB demonstrate extremely high mass activity, that even exceeds the final project target of 0.6 A/mg Pt, and the long-term automotive target of 1.1 A/mg Pt, albeit in RDE testing and at small levels of preparation.

In the longer term, high mass activity and high stability are expected from the complementary routes to Pt thin film deposition being developed on carbon fibre-carbon nanotube electrodes, transition metal doped carbons and NbTiOx-tie layer protected carbon fibres and particles. In addition, the further optimisation of the composition and processing of ultra-low Pt Fe-NC hybrids is expected to continue to extend the frontiers in the activity and stability of this class of catalysts.
All the catalysts and supports under investigation will be further progressed in the coming months and will be screened using the stage-gate criteria.

2. EXPERIMENTAL APPROACHES, RESULTS AND DISCUSSION

2.1. Task 3.2. Corrosion-resistant supports and tie-layers

Carbon corrosion remains as one of the primary challenges for fuel cells to meet the durability targets for automotive applications. This is because the fuel cell stack might be exposed to high voltages i.e. 1.5 V vs RHE, in particular during start up and shut down, and this leads to severe carbon corrosion. Consequently, the life time of the fuel cell stack is reduced and mitigation strategies are needed to prevent this from happening. Therefore, supports with high electronic conductivity and with good stability are still needed. The use of doped carbon supports with conducting oxides deposited via atomic layer deposition (ALD) thin film approaches has been successfully catalysed with Pt via ALD. This approach has proven to give benefits compared to un-doped carbon black supports in terms of performance and stability. Task 3.2 aims for development of corrosion resistant supports and tie-layers. Support materials include nanoparticles and fibres comprising carbons, oxides and carbides. Novel tie-layers are used to improve 1) the stability of, especially, carbon based support materials, and 2) wetting of the surface, i.e. to enhance spreading of the Pt metal added via ALD. VTT has focused on development of carbon based supports and optimisation of tie-layers, while JM has focused on transition metal doped carbons.

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VTT contribution

Precursors for carbon supports were produced by electrospinning of polyacrylonitrile (PAN) and its mixtures with carbon nanotubes (CNTs). Structural properties of electrospun webs were altered e.g. by changing process parameters, and by after-treatments of spun webs using solvent and pressure.

The experimental plan for the tie-layer study was designed by cooperation between JM and VTT. The main variables were Ti-Nb ratio, oxide layer thickness and annealing temperature.

Substrates for VTT’s experimental design included, in addition to carbonised electrospun fibres, various other substrates due to the specific requirements of different analysis methods. Analysis methods include conduction properties (in-plane, through-plane, AFM mapping, EIS studies), surface composition (EDS, TOF-ERDA), surface roughness (AFM), and crystalline structure (XRD).

VTT has invested in a new set-up for coating powders by ALD technology. Coating of particles is based on either conventional flow-through or fluidised bed reactor set-ups. For INSPIRE, a conventional particle deposition set-up with ultrasonic particle stirring was assembled with a Picosun R-200 ALD reactor. Trials were carried out for carbon particles provided by JM. In order to obtain sufficient precursor amount to uniformly coat the powders, 50-100 micropulses (each of 0.1 s) were applied in one cycle. After each set of micropulses, a 200-300 s purge was carried out prior to the next set of precursor pulses.
Work in the INSPIRE project is partly the continuation of work started in CATAPULT (FCH-JU, No 325268) related to fibrous corrosion-resistant catalyst support materials. Those materials were based on carbonised electrospun core fibres and Ti-Nb-oxide tie-layers produced by ALD. The focus can be divided into three topics that are described in more detail below. The topics, main targets, approaches used and outcomes so far are summarised in Table 1.

### Table 1. Summary of VTT work in Task 3.2: topics, targets, approach and outcome so far.

<table>
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<tr>
<th>Topic</th>
<th>Main targets</th>
<th>Approaches</th>
<th>Outcome so far</th>
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<tr>
<td>1. Further development of fibrous carbon supports.</td>
<td>To densify carbon fibre structures by fusing fibres and reducing pores</td>
<td>Changing electrospinning conditions, mechanical pressing and treatment with solvent.</td>
<td>Structure adjustment by changing parameters proved difficult, testing other approaches still to be done.</td>
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<td>To reduce fibre diameter to increase active surface and porosity.</td>
<td>Changing solution composition by reducing polymer content and adding carbon nanotubes (CNTs)</td>
<td>Inclusion of CNTs and reduced polymer concentration did reduce fibre diameters.</td>
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<tr>
<td>2. Fundamental study of Ti-Nb-oxide tie-layers.</td>
<td>To understand conduction behaviour of composite oxide and determining optimal tie-layer properties.</td>
<td>Experimental plan with variables: Ti-Nb ratio, layer thickness, annealing T and making Nb rich top layer. Different support structures were used to enable multiple characterisation methods.</td>
<td>Characterisation of conduction is challenging, e.g. 4-point probe not suitable for this. Characterisation and analysis of results is still ongoing.</td>
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<tr>
<td>3. Production of Ti-Nb-oxide coated carbon materials for Pt coating trials.</td>
<td>To produce good samples interesting for subsequent catalyst studies.</td>
<td>Produce samples including carbonised electrospun fibres as well as commercial carbon fibres and particles.</td>
<td>Work ongoing, awaiting results from stage 2</td>
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**Further development of fibrous carbon supports:** The benefit of electrospun carbon fibre based supports is that in theory they can be used in an MEA as sheets with no need to mill them and make an ink. In practice, the thickness of the sheets has been closer to 20 µm while the targeted thickness has been closer to 10 µm and their z-direction conductivity and active surface area for ionomer deposition was proven insufficient. By densifying the electrospun sheets we wanted to improve the z-directional conductivity of the sheets as well as make the sheets thinner.

Denser structures can be obtained by collecting electrospun fibres whilst partly wet. The resulting structure can be more membrane-like with fused fibre crossings and thus better z-directional conduction. We changed electrospinning parameters such as voltage and distance from needle to the target in order to produce a fused structure by reducing drying of the solution jets during the
electrospinning process. This proved to be very challenging since the window for operation was small. There is a slight variation of electric field and atmospheric conditions in the VTT electrospinning chamber, and we were not able to produce sheets with a homogeneous level of fusion of fibres all over one sheet.

Mechanical pressing of the deposited sheet was tested with elevated temperatures up to 200 °C. Heating and pressing did not melt the fibres together; only a few fibres were flattened during the process. Furthermore, different solvent treatments were applied to the deposition. Firstly, samples were exposed to DMF-vapour from one side of the sample. This procedure did not affect the fibres. Secondly, samples were exposed to DMF-vapour inside the closed cavity at 22 °C (1 day), 60 °C (20 min) and 100 °C (10 min). DMF-vapour melted the fibres at elevated temperatures, but produced uneven areas within the samples (loose fibres, a dense, desired structure and impermeable film). Thirdly, samples were quickly dipped into DMF and then dried. Some fibre crossings were melted together on the sample surface. In retrospect, dipping of the sample into the DMF followed by pressing might have been the most promising technique, but it was not tested.

**Fundamental study of Ti-Nb-oxide tie-layers:** Conduction in-plane has been determined on all samples before and after annealing, and the 4-point method seems not to be suitable for this kind of sample. Results have been contradictory and/or the effects of different treatments do not show any difference in results. There is the possibility to determine conductivity of the samples with an automated 1-point method, and this will studied further in the future.

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**Figure 2.** a) AFM topography image of HOPG without and with 20 nm ALD coatings before annealing, and b) XRD diffractogram of Ti:Nb 1:1 oxide.
Further characterisation and analysis of results are currently ongoing. AFM topography imaging showed the effect of ALD coating on the surface roughness of the samples (see Figure 2a as an example). XRD showed the presence of $\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_2$ mixed oxide when coating with a 1:1 Ti:Nb ratio (see Figure 2b as an example), while only the TiO$_2$ anatase form was typically prominent in 10:1 ratio coatings. It seems that some treatments and characterisation methods may have some unwanted effects on the oxide layer, especially on smooth surfaces such as glassy carbon. Therefore care must be taken to ensure what has been characterised and in interpretation of results.

**Production of Ti-Nb-oxide coated carbon materials for Pt coating trials:** Using ALD deposited Nb-Ti-O for protection of carbon support materials has been previously demonstrated (CATAPULT) and the materials optimisation is being continued in INSPIRE. In addition to protecting conventional fibrous electrospun substrates, there is interest to use ALD Nb-Ti-O for other high surface area materials.

ALD coating experiments with 50 micropulses and a 200 s purge time showed that the topmost 1-2 mm of the substrate powder had a different colour to the rest of the material bed. According to SEM-EDX there was significantly more Ti at the topmost part of the particle bed than at the bottom, indicating either an insufficient amount of TiCl$_4$ or H$_2$O (incomplete reaction) or too short purging time (uncontrolled CVD type growth at the topmost layer). SEM imaging showed that the particle size at the top of the coated substrate bed was markedly increased compared to the bottom of the bed.

In order to obtain uniform coating, the purging time was increased (to avoid CVD growth) from 200 s to 300 s and, at the same time, the number of micropulses was increased from 50 to 100 to ensure a sufficient precursor dose. In order to keep the deposition time relatively short, only 50 deposition cycles were carried out. According to SEM-EDX measurements, the Ti signal from samples collected from the top and the bottom of the bed were close to each other, indicating more uniform TiO$_2$ coating. At the same time, the Ti-signal intensity was only half that of the previous sample, indicating roughly half of the film thickness (as it should be when number of deposition cycles was decreased from 100 to 50). In addition, uniformity seemed improved although there were still some differences in TiO$_2$ morphology when measured in the flow direction of the precursor gases.

Next experiments will be carried out with lower surface area powders and an optimised Nb-Ti-O composition, once optimal structure and composition is confirmed from the fundamental study of Ti-Nb-oxide tie-layers.

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**JM contribution**

**ALD tie-layers on carbon black supports:**

Work prior to INSPIRE has shown that platinum deposited by atomic layer deposition (ALD) onto doped titania, also deposited by ALD, shows promise as an ORR catalyst for a fuel cell cathode. In particular, very high levels of stability to electrochemical cycling have been seen.

Outside the INSPIRE project, JM has contracted two external companies to deposit oxide tie-layers onto a standard JM carbon black support with ALD. Tens of grams of material have been generated by both
groups, with two variants received. The conductivity of the powders was determined both before and after annealing in a reducing atmosphere. In all cases, the conductivity of the coated powders was lower than the base carbon. This was as expected as the oxide should not be conductive prior to reductive heat treatment and after heat treatment the oxide is not expected to be as conductive as carbon alone.

Therefore, it was expected that the more the carbon was coated the lower the conductivity. This appears to be borne out in one of the materials where Variant 2 at the higher oxide loading had a significantly lower conductivity than Variant 1 and the base carbon. On annealing, the conductivity of the more highly loaded material rose significantly, confirming that a large amount of the conduction appears to be taking place through the oxide phase, thus implying that the carbon was well coated. The conductivity of this material was around one quarter that of the base carbon. For a non-carbon material this conductivity is acceptable, but it may have performance implications in the cell. Variant 1 showed a slight decrease in conductivity on annealing suggesting that its conduction is not through the oxide phase and therefore that this material was not conformally coated. The decrease in conductivity may suggest that the oxide coating spreads on annealing, thus covering more of the more conductive carbon.

On the basis of these results, Variant 2 was selected to be catalysed and tested in Task 3.3.

**Modified carbon supports via wet chemical methods.** In Task 3.2, JM also explored the synthesis of modified carbon supports with the use of transition metals (TMs). Therefore, a library of carbon doped-TMs were produced and annealed in an attempt to create a modified support with better corrosion resistance and Pt adhesion. The metal loading of the TM dopant was around 10% and seven transition metals were explored. The modified carbons were annealed at different temperatures under oxidising or reducing atmospheres. The different catalyst powders were characterised by XRD in order to obtain experimental evidence of successful incorporation of the TM to the carbon support. In addition, these modified carbon supports were tested for chemical stability by stirring the modified carbon powder in acid for 24 h and 80 °C. The leachate was analysed via ICP-MS to quantify if any of the added transition metal was leached to the acid. Out of this work, five modified TM carbon supports were transferred to Task 3.4 for Pt addition via wet chemical methods.
2.2. Task 3.3. Electrocatalyst film deposition

CNRS contribution

Other strategies that can lead to active and stable catalysts are based on the synthesis of contiguous thin platinum films on different substrates such as metals, polymers or fibres. Galvanic exchange is a highly significant strategy in the search for new advanced electrocatalysts; in particular the galvanic displacement of a non-noble metal by platinum has been widely adopted as one of the go-to synthetic approaches for the preparation of highly active electrocatalysts based on core-shell morphologies.\(^1\)\(^-\)\(^6\)

Core-shell nickel-platinum nanofibrillar catalysts are considered a possible high performing alternative catalyst to conventional carbon platinum nanoparticles for cathode application. Produced by a galvanic displacement reaction of nickel by platinum in aqueous solution this catalyst has demonstrated outstanding mass activity in oxygen reduction reaction\(^7\). This fibrous catalyst is typically composed by a nickel core fully covered by a thin layer of platinum; it is possible during synthesis to control the platinum layer thickness but continuous layers thinner than 2-3 nm have not yet been demonstrated.

One of the major technical barriers that hinders the adoption of the galvanic displacement reaction of nickel with platinum is the difficult scale-up and the long reaction times required (~8 hr at 80 °C)\(^6\),\(^8\). Microwave irradiation is an effective energy delivery method leading to metal nanoparticles, and nanofiber synthesis\(^9\), welding\(^10\), nanoparticle synthesis\(^11\)\(^-\)\(^16\) and sintering\(^17\),\(^18\) have all taken advantage of microwave irradiation as the energy source.

In the previous FCH JU project CATAPULT we studied the feasibility of using microwave irradiation as the energy source for the galvanic displacement of platinum over nickel and were able to successfully reduce the reaction times by a factor of over 200, so reducing the total time of reaction to only 2 minutes. During the first 14 months of INSPIRE, the major parameters controlling the reaction were evaluated and a deeper understanding and a more efficient control of the different aspects of microwave assisted galvanic displacement reaction were gained. We could effectively and efficiently control the platinum loading on the nickel fibres and achieved a total conversion of platinum precursor to metallic platinum in the nanofibrinous catalyst eliminating platinum costs overhead of the galvanic process.

In this Task 3.3, core-shell nanofibrous catalysts were prepared by microwave assisted galvanic displacement with different defined platinum loadings and fully characterised by TEM, ICP-MS and XRD. The platinum electrochemically active specific surface area, the specific activity and mass activity towards oxygen electro-reduction, and the stability of the electrocatalysts prepared were evaluated ex-situ in a three electrode cell setup both at the beginning of testing and end of testing. In addition, Pt tubes were also prepared by leaching out the nickel core of the core-shell nanofibrous catalysts in an acid solution; the platinum tubes were characterised in a similar manner to the core-shell catalysts.

All the core-shell catalysts meet the INSPIRE project target for mass activity when evaluated ex-situ.
A second strand in Task 3.3 is the deposition of Pt thin films on conducting nanofibres. During CATAPULT we developed a novel class of electrocatalysts intermediate between carbon black decorated with platinum nanoparticles and existing extended film catalysts that comprised platinum conformally electrodeposited around the carbon nanofibres of a self-standing electrode. We found that by combining two cost-effective and up-scalable techniques, electrospinning and high over-potential electrodeposition, it is possible to obtain an electrocatalyst with outstanding platinum exploitation and high durability while minimising fabrication complexity. We produced electrocatalyst layers with tuneable morphology that could be measured directly and potentially used as such, removing the need to prepare inks in a similar fashion to conventional NSTF (nanostructured thin films) or other 3D macroscopic assembly techniques. These structured 3D electrocatalyst layers have high electrical conductivity for fast charge transport, and hierarchical pores for efficient reactant mass transportation. The carbon nanofibrous electrodes we used comprised polyacrylonitrile (PAN) derived electrospun carbon nanofibres, which we have demonstrated to be a potentially viable alternative carbon support.

In particular, we showed how controlling the pulse length in pulsed electrodeposition could be used to control coverage density and diameter of platinum clusters. The ECSAs we measured for these novel electrocatalysts were up to 120 m²/g, which is higher than most highly optimised commercial catalysts currently available and the stability was up to three times higher than that achieved with conventional carbon-platinum and without the introduction of more stable / less conductive metal oxide supports.

However, integration of the self-standing electrodes in an MEA showed that these catalyst layers, while showing high stability and high platinum specific surface areas, were also characterised by low density, low support surface area and anisotropic connectivity. Ultimately, the combination of all of these translated into MEAs in which proton transport from the deeper layers of the electrodes to the membrane surfaces was difficult, and having low maximum platinum loading (<0.05 mg/cm²).

During the initial period of INSPIRE, attention at CNRS was focused on modifying the layer morphology in order to increase the density, connectivity and surface area of the electrospun carbon nanofibre support.

**Synthesis of PtNi nanowires:** Platinum was exchanged on commercial nickel nanofibres using an aqueous solution of chloroplatinic acid adjusting the pH to the target value using hydrochloric acid or oxalic acid. The solution was irradiated for 120 seconds in a microwave (MW) reactor at 200 W under N₂ atmosphere. At the end of this time, the nanofibres were collected by filtration and carefully washed multiple times.

A nickel oxide passivation layer is usually present on the surface on nickel nanofibres; this oxide layer protects the nickel from further oxidation and prevents a successful galvanic exchange from taking place. Time of reaction, platinum ion concentration and energy delivery methods have no effect in pushing the exchange and the final platinum loading is limited to a maximum of 2-3 wt%. As a matter of fact this passivation layer removal is the first step necessary to drive the exchange to proceed until complete utilisation of the platinum ions in solution and to achieve the desired Pt loading. Hydrochloric acid addition to the exchange solution was successfully adopted to push the exchange towards higher resulting platinum loadings in thermally activated galvanic reactions. Using microwave irradiation as the energy delivery method does not change the barrier to reaction effect provided by the passivation layer.
layer and hydrochloric acid addition is an effective method to remove this barrier and achieve platinum loading higher than 3 wt% also when the reaction is conducted in a microwave reactor.

When hydrochloric acid is replaced by oxalic acid, a chelating organic acid, the reaction reaches completion at significantly lower amounts of added acid and gives reliable control of the exchange reaction. The microwave reaction together with the acids addition allows complete exchange of the platinum ions in solution, and is thence possible to assume that control of the final platinum loading is achievable by tuning the platinum ion concentration. To validate this assumption a set of exchanges targeting different final platinum loadings was conducted both with the addition of hydrochloric acid and oxalic acid, and the final platinum loading was measured by ICP-MS. The XRD diffractograms measured for the samples at different platinum loadings obtained using oxalic acid clearly show the presence of crystalline platinum and crystalline nickel.

The platinum shell thickness can be controlled by changing the platinum loading, and an example is provided in Figure 3. The STEM-EDX map overlaid onto the bright field images provides strong evidence for the presence of a thin conformal Pt coating, the thickness of which increases with increase in Pt content. The EDX line scans bestows additional evidence that Pt is confined to an outermost layer and is not alloyed with the nickel core.

![Figure 3. TEM-EDX mapping of platinum (red) and nickel (green) overlay on STEM bright field images of nickel platinum core-shell nanofibres with 25 wt.% platinum loading. EDX line scans analysis are shown in situ.](image)

ECSA, mass activity at 900 mV<sub>RHE</sub> and specific activity at 900mV<sub>RHE</sub> were evaluated by ex-situ electrochemical analysis in a 3-electrode cell setup. All catalysts have mass activity values ~ 0.50 A/mg i.e. more than twice the INSPIRE standard JM platinum/carbon catalyst (0.23 A/mg at beginning of testing BOT and 0.16 A/mg at the end testing EOT) and also higher than the platinum-nickel-carbon baseline catalyst provided by JM, and they hence achieve the INSPIRE MS2 milestone.

One concern of using with a nickel containing catalyst is the possibility of the nickel leaching during operation and consequently poisoning of the membrane and reduction in MEA performance. To quantify the extent of the nickel leached during the catalyst operation the electrolyte used in the three electrode electrochemistry setup was collected at the end of testing and analysed by ICP-MS. The highest amount of nickel is lost by the low loaded catalyst with a platinum particulate dense coverage of the nickel core (~ 17.5 wt% of the original nickel on the electrode). Catalysts with higher platinum
loadings and thicker shells, while showing smaller quantity of nickel lost, also present a non-trivial amount of nickel in the electrolyte solutions.

A first attempt at minimising nickel dissolution consisted of dissolving the nickel core of the electrocatalyst before testing. In particular, the nickel core of the 25 wt% platinum loading catalyst was removed using 3 M HNO₃. This approach removes the concern of nickel core dissolution by completely removing the nickel core and the catalyst obtained is mainly composed of platinum-nickel nanotubes. Removing the nickel core, while solving the issue of nickel dissolution during operation, results in a lower performing catalyst with lower values of all the relevant parameters. An alternative nickel stabilisation protocol will be applied to reduce the nickel potentially lost during fuel cell operation.

*Thin film Pt electrodeposition on nanofibres:* Polyacrylonitrile (PAN, Mw=150,000, Sigma Aldrich) based carbon fibres were prepared following electrospinning with thermal treatments as already reported.⁴¹-⁴³ Alternatively, for the preparation of carbon nanotubes on carbon nanofibres, metal precursors (0.1 M metal nitrates) were also added to the electrospinning solution.

The produced carbon electrodes were subsequently treated at 80 °C in a 3 M HNO₃ solution for 5 hr. Pt electrodeposition was performed in a 2-electrode setup, where the counter electrode consisted of a 50 x 50 x 0.8 mm graphite foil facing the working electrode and kept 10 mm away; the latter was a 50 x 50 x 0.02 to 0.05 mm carbon nanofibre self-standing web. Both electrodes were immersed in a N₂ saturated 0.1 M H₂PtCl₆ 5H₂O solution and contacted using an electrodeposition cell designed in-house. The deposition voltage was cycled between -3.0 V and 0.0 V vs RHE for the desired number of pulses and duration. Samples were thoroughly washed with deionised water (18 MΩ cm), dried and weighed on a microbalance.

We first investigated the production of aligned carbon nanofibre electrodes for the densification of the support. The aligned carbon nanofibres electrodes were obtained by increasing the rotation speed of the drum collector from the usual 300 RPM to 1500 RPM. The increased rotation speed of the drum generates a draw effect on the fibres, aligning them along the surface velocity vector. Figure 4 displays fibres obtained at 300 RPM and 1500 RPM. A consequence of the alignment is an increase in density of the electrode by around ~ 30 %.

Another possible route to densify the electrodes and reduce the anisotropy of the connectivity is to grow carbon nanotubes from the surface of the carbon nanofibres by doping the latter with CNT growth catalysts and performing a CVD growth during or after carbonisation of the PAN. In a first study we used hexane vapour as a source of carbon for the formation of carbon nanotubes and iron acetylacetonate as iron nanoparticle precursor in the electrospinning solution.
Using this technique, we were able to obtain carbon nanotube-carbon nanofibre (CNF-CNT) electrodes and also control the length of the carbon nanotubes by changing the exposure times to hexane vapour. To increase the yield of the carbon nanotubes, we investigated the growth of carbon nanotubes at 900 °C using ethanol vapour as the carbon source and palladium, platinum, silver, copper, aluminium, iron and nickel catalysts. Iron resulted in straight nanotubes while nickel gave curly ones (Figure 5).

Figure 5. SEM images of carbon nanotubes obtained using either iron or nickel as growth catalysts.
Acid based leaching is capable of completely removing accessible iron. Cyclic voltammetry demonstrates that there is no residual accessible iron after the leaching process, furthermore additional evidence was also obtained by TEM investigation that only showed the presence of embedded iron after the leaching. The embedded iron is completely enclosed in the nanotubes and a layer of carbide is also present on the surface of these iron particles, and therefore there should not be concern for further iron dissolution occurring during MEA operation.

With a reliable and reproducible process defined for the production of multi-layered hierarchical self-standing CNF-CNT electrode with tuneable lacunarity, we were able to begin platinisation by high overpotential electrodeposition, and an example of a platinised electrode is given in Figure 6.

![Figure 6. SEM image of the surface of a platinised CNF-CNT electrode.](image)

Such electrodes will be investigated as cathodes in complete MEAs in the next months of INSPIRE.

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**JM contribution**

Work prior to INSPIRE has shown that platinum deposited by ALD onto doped titania, also deposited by ALD, shows promise as an oxygen reduction catalyst for a fuel cell cathode. In particular, very high levels of stability to electrochemical cycling have been seen. Because of the benefits of this approach undoped and doped carbon supports developed in Task 3.2, have been catalysed with Pt via ALD and compared to Pt/C catalysts made via conventional wet chemistry routes. Highlights of the results of this work are given in this report.

**Pt addition to carbon supports via ALD:** The tie-layer coated carbon support transferred from Task 3.2 was catalysed by a JM proprietary wet chemical route and by Pt ALD. For the wet chemical route, the Pt loading was fixed at 37% Pt on the basis that this would, assuming the oxide coating was conformal on the carbon black give the same Pt particle density as the benchmark 50% Pt/C catalyst.

**Synthesis and electrochemical performance of ALD-Pt /doped-C catalysts:** To allow coating of a powder in the JM ALD tool, which is designed for flat substrates, the carbon support powder modified with an oxide tie-layer was bar coated onto aluminium foil from a water/IPA mix. After drying the powder was
immobilised onto the foil sufficiently to allowing coating in the ALD tool, but due to the lack of any binder the layer could be easily scraped off after the ALD run. The ALD was carried out with the conventional Pt process, namely trimethy(methylcyclopentadienyl) Pt IV and oxygen at a reactor temperature of 300 °C. It was found that the Pt loading on the immobilised powder was reasonably uniform if only one cycle of ALD was used. One cycle is defined as the exposure of the sample to both the Pt precursor then oxygen. If more than one cycle of ALD was used the Pt coverage was very uneven, with only the front edge of the bed being coated. In order to approach the desired loading, many Pt pulses were required. The 30% Pt catalyst made via ALD had a metal surface area of 67 m²/g Pt suggesting that the ALD was giving a very highly dispersed Pt deposit. The wet chemical route used for Pt addition to the same modified tie-layer carbon support gave 48 m²/g Pt with 37%wt Pt loading.

Measurement of the Pt particle size of both catalysts was carried out by TEM. The mean particle sizes were 3.2 nm for the wet chemical sample and 1.8 nm for the ALD sample in agreement with the CO metal area results above.

MEAs were prepared from both catalysts by creating a catalyst ionomer suspension in water/IPA by ultrasonication. This was then airbrushed onto a piece of heated membrane. The Pt loading was determined by XRF mapping of the finished catalyst layer. An anode catalyst layer was then hot-pressed onto the other side of the membrane and the sample cell tested. MEAs were made at 50 cm² and 6 cm². Due to this method of MEA preparation and the limited amount of ALD catalyst available, MEAs were necessarily created at different Pt loadings, the target loading was 0.1 mg/cm² but the ALD Pt layer had less than this. The data shown in Figure 7 is therefore corrected for the loading and the x axis represents catalyst layer mass activity.

![Oxygen Polarisation at 50 kPa](image)

**Figure 7.** Loading normalised oxygen polarisation curves of MEAs made using the ALD oxide coated carbon supports at 50 kPa inlet pressure and 100% RH inlet.

The oxygen polarisation data above shows that both MEAs function quite well, although there is a clear performance benefit of the chemically catalysed sample. The electrochemical surface area (ECSA) measured in the cell was in good agreement with the ex-situ gas measured area for the case of the chemically catalysed sample but the ALD catalyst displayed less than half the area that would be
expected from the gas phase measurement. The reasons for this are unclear, but this will reduce the performance significantly. The increase in MEA resistance apparent from the increased slope and curvature of the polarisation curve for the ALD sample in Figure 7 could imply that the relatively poor conductivity of the coated carbon support is causing iR losses in the cathode catalyst layer and thereby reducing performance. This possibility is, however, excluded by the fact that the curve for the chemically catalysed sample follows the expected log-linear behaviour. It appears therefore that the conductivity of the support is adequate for application in a fuel cell. Thus the reason for the increased resistive losses for the ALD sample is not the intrinsic conductivity of the support but probably related to the structure of the layer. Given that the ionomer could only apparently access half the ALD Pt it may be that this loss is protonic in nature due to some problem in ionomer/support interaction.

The main motivation for the use of this support was the previously observed (CATAPULT) stability of platinum to electrochemical cycling. This was tested by cycling the ALD sample 30,000 times between 0.6 – 0.925 V vs RHE (protocol defined in detail in INSPIRE deliverable 3.1). The CO peaks from the cyclic voltammograms taken before and after this cycling gave evidence of a faster decrease in surface area compared to the benchmark catalyst; it appears that the ALD sample is not more stable in this case. This result shows that ALD Pt on the oxide tie-layer does not always form the highly stable form of platinum seen previously.

In order to better understand the nature of the Pt/tie-layer interface a series of doped TiOx coated Si wafers were prepared by VTT and annealed at JM. In order to not be limited by the in-plane resistance of the oxide tie-layer the oxide was coated onto a highly conductive sputtered gold layer covered with carbon (Figure 8). The carbon layer was used to encourage the tie-layer to have similar growth characteristics and morphology to when it is deposited onto particulate carbon.

![Figure 8. Schematic diagram of Pt coated via ALD on to doped Ti-Ox silicon wafers with a gold interlayer.](image)

It was hoped that by depositing Pt onto these substrates by ALD and then characterising the Pt-coated samples by cyclic voltammetry, the nature of the electrochemical behaviour of the Pt deposit, in response to the tie-layer variables described above under Task 3.2 above (VTT section), could be better understood. Clearly, the aim was to identify the tie-layer properties that can lead to highly active and stable Pt deposits.
A series of cycles of Pt ALD were carried out onto a sample with 20 nm of doped-TiOx with a Ti:dopant ratio of 1:1. The in-plane conductivity of this sample, as determined by four-point probe measurements, was sufficiently high to suggest that this had formed a percolating film of platinum on the surface of the doped-TiOx. Initial attempts to characterise this sample by cyclic voltammetry in dilute sulphuric acid were unsuccessful. No meaningful features were observed in the voltammogram even after extensive voltage cycling. Ex-situ cleaning of the sample using dilute “Piranha” solution (sulphuric acid and hydrogen peroxide) removed what must have been a layer of organic contamination and allowed a voltammogram in good agreement with polycrystalline Pt to be obtained. A sample with half the ALD cycles of Pt was then prepared on a sample with 10 nm of doped-TiOx 1:1; this had a significantly lower in-plane conductivity suggesting that in this case the Pt film was not percolating. Attempts to measure a voltammogram from this sample were unsuccessful, even after directly dosing the sample with “Piranha” solution. From the lack of features in the voltammograms it appeared that the resistance of the sample was so high that it inhibited the electrochemical cleaning process such that a clean Pt surface could not be obtained. It is not currently clear how this problem can be solved to allow electrochemical characterisation of the Pt/doped-TiOx system and further work is in progress.
2.3. Task 3.4. Extended activity/durability alloy nanoparticle catalysts

**TUB contribution**

Based on studies on single crystal surfaces, (111) exposing Pt-Ni particles are predicted to be highly active for the oxygen reduction reaction (ORR).\(^{35}\) Indeed, high initial activity is observed on state of the art octahedral PtNi nanoparticles.\(^{36-37}\) Despite this high initial performance, some challenges remain to be met: morphological stability under electrocatalytic conditions and a higher Pt mass normalised electrochemically active surface area (ECSA). Reducing octahedral particle size is expected to improve the ECSA, while alloying the surface with a third element has recently been reported as a promising method to preserve the octahedral shape.\(^{38-40}\) In this task, octahedral PtNi alloy nanoparticles with size smaller than 9 nm have been investigated and Mo surface doping has been applied. The synthesis of carbon supported octahedral PtNi alloy nanoparticles has been carried out using autoclaves and a solvothermal method which constitutes a modification of previously published methods.\(^{37,38}\) The Mo surface doping is accomplished by a subsequent solvothermal treatment applied to the previously synthesised octahedral PtNi nanoparticles.\(^{38}\) The total catalyst amount produced in a synthesis is typically ~ 80 mg. The catalyst is then characterised with X-ray diffraction (XRD), inductively coupled plasma spectroscopy (ICP) and transmission electron microscopy (TEM). Finally, the activity and stability of the catalyst is tested using a rotating disk electrode (RDE) setup according to the protocol developed inside the INSPIRE project.

![Figure 9. TEM images of Pt\(_{71}\)Ni\(_{29}\)/C (a), Pt\(_{67.5}\)Ni\(_{31.6}\)Mo\(_{0.9}\)/C (b) and Pt\(_{66.63}\)Ni\(_{31.92}\)Mo\(_{1.45}\)/C (c). In Figure c), two octahedral nanoparticles are circled in blue, smaller cubooctahedra in red and agglomerates in purple. XRD of the three catalysts with reference patterns for Ni and Pt fcc phases (d).](image-url)

\(^{35}\) Similar to previous studies.\(^{36}\) This is a promising method.\(^{37}\) The total catalyst amount produced in a synthesis is typically ~ 80 mg. The catalyst is then characterised with X-ray diffraction (XRD), inductively coupled plasma spectroscopy (ICP) and transmission electron microscopy (TEM). Finally, the activity and stability of the catalyst is tested using a rotating disk electrode (RDE) setup according to the protocol developed inside the INSPIRE project.
Octahedral PtNi and PtNiMo nanoparticles were successfully synthesised with an average size of ~7 nm, smaller than the most common size of ~9-10 nm reported for many state of the art octahedral Pt alloy nanoparticles, (Figure 9a-c).

On the other hand, some smaller undesired cuboctahedra and agglomerates are present. A strategy for improving the yield of octahedral particles is currently under investigation that involves modification of the carbon supporting step and optimisation of the loading. Figure 9d shows the XRD of three catalysts with similar Pt/Ni ratio but different Mo content. All of them display patterns typical of lower Ni content single-phase alloys.

![Figure 10. Cyclic voltammetry (a) and linear sweep voltammetry (b) of Pt_{67.5}Ni_{31.6}Mo_{0.9}/C catalyst before (black) and after (red) stability protocol. The arrow in (a) points to feature typical of Pt(110) surfaces, suggesting some degree of facetting. Vertical lines in (b) indicate potentials where the activity is conventionally and most commonly evaluated.](image)

The three catalysts show similar qualitatively cyclic voltammetry (Figure 10a), which develop some degree of facetting after the stability test. The catalyst films display excellent RDE film and kinetic data quality (Figure 10b), with diffusion limited current in agreement with theoretical predictions.

![Figure 11. ECSA (a) and Mass activity (b) for Pt_{71}Ni_{29}/C, Pt_{67.5}Ni_{31.6}Mo_{0.9}/C and Pt_{66.63}Ni_{31.92}Mo_{1.45}/C. Values before (blues) and after (red) the stability protocol are reported. The dashed green lines in (a) and (b) shows the desirable ECSA of 50 m^2/gPt and the target mass activity of two times the reference Pt/C catalyst (~0.54 A/mgPt).](image)
Figure 11a and 11b report the ECSA and the mass activity, respectively. The ECSA shows values in the range between 30 and 50 m$^2$/g Pt. The sample with lower and higher Mo content have Pt wt% on carbon of 21.5 and 17.9 and higher ECSA than the catalyst with intermediate Mo content, which has a Pt wt% of 29.7. This suggests that a Pt wt% loading of ~20 is optimal for this kind of catalysts. ECSA close to 50 m$^2$/gPt (dashed line) or higher provides good indication for avoiding big losses due to O$_2$ local diffusion resistance at high current density and low Pt loading. Reducing agglomeration might improve the ECSA value even further. The increase of ECSA after stability tests is due to roughening and faceting of the nanoparticles. The mass activities (Figure 11b) are all well above the target of two times the activity of Pt (dashed line) and increase with Mo content. In particular, the best performing sample shows an extraordinary high initial mass activity of 3.7 A/mg_{Pt}. The activity decreases after stability tests probably due to the observed faceting, but still remains above the target.

**JM contribution**

Dealloyed catalysts PtM$_x$/C, M=Cu, Ni or Co and x=1 to 3, have demonstrated very high mass activities in RDEs and MEAs, which exceed the US DOE mass activity target of 0.44 A/mg Pt. These formulations have been explored in industry and can be scaled up to large volumes. Despite their excellent mass activity key challenges remain unsolved. The first is the integration of these catalysts into catalyst layers that can produce power densities $>$ 1.0 W/cm$^2$. The second main challenge for dealloyed catalysts is to meet the durability target in membrane electrode assemblies (MEAs) under H$_2$/Air. This is particularly challenging because metal dissolution is very difficult to prevent during operation and the leached metal ions can reduce performance. Therefore, in this task we have focused on the synthesis of dealloyed PtNi/C catalysts that are capable of overcoming these challenges with a particular emphasis on improving catalyst surface area and reduction of nickel dissolution during operation.

Briefly, for the synthesis of dealloyed PtM/C alloy catalysts, the carbon is slurried in weakly basic water before addition of the metal salts. On complete deposition of the metal, the metal was reduced either by chemical methods or by heat treatment under a reducing atmosphere at different temperatures. The catalyst powders were then acid washed to remove excess nickel and afterwards washed in water until the conductivity of the leachate was below 10 S. Alloying of the Pt/Ni catalysts was confirmed by the presence of a PtNi phase using XRD analysis with a Bruker AXS D-500 Diffractometer. XRD crystallite sizes were determined for each catalyst. Measurement of catalyst metal surface area) was determined from gas phase chemisorption with carbon monoxide. Electrochemical surface areas were measured via cyclic voltammetry in a fuel cell using the CO desorption area, using a correction factor of 420 μC/cm$^2$ Pt. Measurements for catalyst activity and stability in single fuel cells were described in detail in Deliverable 3.1.

A series of dealloyed PtNi/C catalysts were produced at JM on two different carbon supports and using three different synthesis routes. These are summarised in Table 2.
Table 2. Catalyst formulations explored in Task 3.4.

<table>
<thead>
<tr>
<th>Catalyst key</th>
<th>Synthesis type</th>
<th>Carbon type</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Benchmark Pt</td>
<td>Pt synthesis 1</td>
</tr>
<tr>
<td>B</td>
<td>PtNi (Reference alloy in WP3)</td>
<td>Alloy Synthesis 1</td>
</tr>
<tr>
<td>C</td>
<td>New Pt route</td>
<td>Pt synthesis 2</td>
</tr>
<tr>
<td>D</td>
<td>PtNi</td>
<td>Alloy Synthesis 1</td>
</tr>
<tr>
<td>E</td>
<td>PtNi</td>
<td>Alloy Synthesis 2</td>
</tr>
<tr>
<td>F</td>
<td>PtNi</td>
<td>Alloy Synthesis 3</td>
</tr>
<tr>
<td>G</td>
<td>PtNi</td>
<td>C2</td>
</tr>
<tr>
<td>H</td>
<td>PtNi</td>
<td>C2</td>
</tr>
</tbody>
</table>

As shown in Table 2, alloy catalysts were synthesised on two different carbon supports labelled C1 and C2. The difference in the carbon supports is their stability against corrosion when taken above 1.0 V vs RHE, C1 being more corrosion tolerant than C2. In addition, three different synthesis routes with different PtNi compositions were explored, as shown in Table 2. The aim of this matrix of samples was to optimise the properties of the alloy catalysts to meet the performance targets at low and high current density. In order to validate these different formulations, catalysts were screened first for activity and stability at JM in 6 and 50 cm² single cells in H₂/O₂. This first screening tool under H₂/O₂ is primarily designed to discard catalysts that are not significantly better, in terms of mass activity, than the benchmark catalyst. The catalysts that meet the criteria can proceed to further analysis in larger MEAs and eventually progress to Task 3.6 for initial catalyst layer development. Several of those materials that passed the initial screening appear in Figure 12, which shows the measured catalyst mass activity in 50 cm² MEAs under H₂/O₂ before and after durability testing under H₂/O₂ vs benchmark catalyst A.

Figure 12. Measured mass activities before and after durability test in 50 cm² single fuel cell. Catalysts were cycled between 0.6-0.925 V vs RHE for 30,000 cycles in H₂/N₂ at 80°C. The mass activity was measured at 0.9V and the values quoted are iR free. The blue and black bars show the catalyst mass activity before and after durability cycling respectively.
Results show that all the alloy catalysts exceed the mass activity of the benchmark catalyst before and after durability testing. However only catalysts B, D and G exceed the Pt/C catalyst by nearly a factor of 2. Catalyst F did not show 2xPt activity benefit but produced good stability and was also considered as a promising candidate. Therefore, the alloy catalysts B, D, F & G were progressed to characterisation under H₂/Air in 50 cm² cells.

Figure 13 shows the performance of catalysts F and G under H₂/O₂ and H₂/Air. The results show that the performance of both catalysts under H₂/O₂ is significantly better than the Pt/C benchmark (A) catalyst layer at all current densities. Under H₂/Air, these two alloy formulations performed better than Pt/C benchmark catalyst layer below 1.2 A/cm² and 1.8 A/cm² for catalysts G and F respectively. The decrease in performance observed at higher current densities is thought to be due to differences in the synthesis approach used (Table 2) which lead to different catalyst layer structures. Therefore the gas and liquid transport are affected, which results in decrease in performance at high current density. Figure 13, clearly shows that different carbon supports can lead to very good activities at low current density under H₂/Air (< 1.0 A/cm²). However, the differences in layer structure are evident at higher current densities and under these conditions, catalyst G despite out-performing the benchmark catalyst at most current densities, was significantly poorer than the benchmark catalyst layer above 1.2 A/cm².

Catalyst C, made using a new Pt/C synthesis, performed as well as the benchmark catalyst A under these conditions. On the other hand, PtNi alloy catalysts (B & D) did not improve against the benchmark catalyst under H₂/Air and were lower in performance than the PtNi catalysts F & G.

![Figure 13. Performance under H₂/O₂ and H₂/Air at 80 °C, 100% RH and 100 kPa, for alloy catalysts F (red line) and G (blue line) compared to Pt/C benchmark A (black line).](image-url)
under H\textsubscript{2}/Air. Hence, due to the good performance observed, the new PtNi catalysts (F & G), in addition to Pt/C catalyst C, were progressed to Task 3.6 for further catalyst layer optimisation.

Within Task 3.4, JM also explored the performance of Pt catalysts coated on transition metal (TM) doped carbon supports developed in Task 3.2. Table 3 shows the range of the gas phase metal areas measured for the different modified supports compared to the unmodified carbon black support.

Table 3. Surface areas measured by gas phase CO chemisorption for the modified-TM supports and un-doped carbon support. The metal loading of the TM dopant was around 10% and the Pt loading was kept at 30 wt%.

<table>
<thead>
<tr>
<th>TM doped carbon initial</th>
<th>TM doped carbon post annealing, Pt SA m\textsuperscript{2}/g (intermediate Temp, reducing atmosphere)</th>
<th>Un-doped carbon initial</th>
<th>Un-doped carbon post annealing, Pt SA m\textsuperscript{2}/g (intermediate Temp, reducing atmosphere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt SA m\textsuperscript{2}/g</td>
<td>84-74</td>
<td>76-60</td>
<td>85-76</td>
</tr>
<tr>
<td>%loss of surface area (6-21)</td>
<td>%loss of surface area (6-18)</td>
<td></td>
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</tr>
</tbody>
</table>

Table 3 shows that the Pt surface area is not significantly lower on the TM-doped carbon supports compared to the un-doped support. This was a good initial step as it is commonly observed that lower surfaces areas are reported on modified carbon supports. After XRD and TEM analysis, two Pt / TM-doped carbon catalysts were selected as suitable candidates for performance testing. It was observed that the interaction of the ionomer with these modified carbon supports was significantly different from that with the un-doped support, as might be expected. Different ink compositions were attempted and catalyst layers were produced on PTFE sheet. It was observed that poor coatings were produced when Pt loadings of 0.20 mg Pt/cm\textsuperscript{2} were targeted, due to the intrinsic interaction of the ionomer with the Pt catalyst and the carbon support. However good quality catalyst layers were obtained with 0.10 mg Pt/cm\textsuperscript{2} loadings. Table 4 shows the results from testing in a 50 cm\textsuperscript{2} single cell.

Table 4. Characterisation of Pt catalysts on modified carbon supports compared to benchmark catalyst. Cathode loading for the Pt / TM-C (1) & (2) was fixed at 0.10 mg Pt/cm\textsuperscript{2} and the benchmark catalyst was 0.2 mg Pt/cm\textsuperscript{2}. Measurements reported under H\textsubscript{2}/Air at 80°C, 100%RH and 100kPa inlet.

<table>
<thead>
<tr>
<th>Catalyst key</th>
<th>Catalyst layer loading (mgPt/cm\textsuperscript{2})</th>
<th>Electrochemical surface area (CO) (m\textsuperscript{2}/gPt)</th>
<th>E cell / V at 1.6 A/cm\textsuperscript{2} and 100% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt / TM-C (1)</td>
<td>0.1</td>
<td>75</td>
<td>0.54</td>
</tr>
<tr>
<td>Pt / TM-C (2)</td>
<td>0.1</td>
<td>73</td>
<td>0.42</td>
</tr>
<tr>
<td>Pt/C benchmark</td>
<td>0.2</td>
<td>53</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Initial results show that Pt / TM-C (2) shows significantly lower performance compared to the benchmark catalyst at high current density. This was due to poor interaction of the ionomer with the catalyst powder. However, Pt / TM-C (1) gave promising initial performance considering that the Pt loading used in the layer was half that of the benchmark catalyst. This formulation Pt / TM-C (1) was
tested for durability using the protocol described in detail in deliverable D3.1. Results show that this formulation performed as well as the benchmark catalyst but that no stability benefits of the modified support were observed. A durability test at higher voltages (i.e. 1.0 – 1.5 V vs RHE) might reveal the benefits of the TM-C compared to the un-doped support. This is ongoing and if successful, this type of doped support will be catalysed with an alloy catalyst.

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**TUM contribution**

The aim of the studies at TUM is electrochemical deposition of Pt-rare earth (Pt-RE) catalysts from ionic liquids (ILs). In earlier work, within the CathCat project, the enhanced activity of Pt-RE catalysts had been demonstrated. Both La and Pt had been successfully deposited using ionic liquids. The main advantages of ionic liquids are a wide electrochemical window permitting to carry out reactions outside the stability window of water, their non-flammability, a nearly non-existing vapor pressure permitting operation even in UHV, and often low toxicity. However, strong interfacial layers in ionic liquids can hinder deposition process. This effect could be mitigated by either addition of small ions such as Li ions or by use of higher temperatures. In this task so far, the main focus of the experimental work carried out was on the electrodeposition of Gd and its further optimisation.

Different ionic liquids and Gd precursor salts were tested for electrodeposition experiments. Both experiments at room temperature as well as at elevated temperatures were carried out. For the latter, a special glass cell for the EQCM measurements in the glovebox was constructed. All potentials in this work are measured versus a Pt quasi reference electrode. Two types of potentiostats were used, on the one hand an Ivium Plus CompactStat, and on the other hand a Solartron SI 1287. In most electrochemical experiments, one of the two Au contact electrodes of a quartz resonator (KVG quartz crystal technology) for the electrochemical quartz crystal microbalance technique (EQCM) served as working electrode. A network analyzer (Agilent E5100A) was used to measure the electrical admittance of the quartz in the vicinity of the resonance frequency in parallel to the electrochemical measurements. From a Lorentzian fit to the real part of the admittance, both resonance frequency and damping of the quartz were determined. Pt wires (99.99%, MaTeck GmbH) served as the reference and counter electrodes. In earlier experiments also highly oriented pyrolytic graphite (HOPG, grade ZYB, Mikromasch) was used as the substrate, especially for Pt deposition from chloroplatinic acid hexahydrate (H₂PtCl₆ x6H₂O, 99.995 %, Sigma Aldrich).

**Short overview of previous results.** Within CathCat, Pt nanoparticles had been deposited successfully from two different ionic liquids, namely 1-N-octyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imid and N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate, using H₂PtCl₆ as Pt precursor. Similar to literature reports, Pt deposition was a two-step process as evidenced by two cathodic peaks in the cyclic voltammograms. Potentials of -1.5 V with respect to a Pt quasi reference electrode were required for Pt metal deposition. AFM measurements showed particle sizes as small as 4 nm. Experiments in aqueous sulphuric acid had demonstrated both typical Pt CV characteristics and catalytic activity for the ORR. Y deposition was not successful, even though many interesting results on the electrochemical behavior had been obtained. La deposition was tried from two different precursors, La(NO₃)₃ and La(TFSI)₃. Even though deposition had been claimed in literature with the former precursor, these results could not be reproduced. The latter precursor...
permitted deposition, but at relatively low rates\(^9\). As the electrochemistry of Gd and La should be quite similar, and Pt-Gd alloys represent the best choice among all Pt-RE catalysts regarding activity and stability\(^7\), the focus in INSPIRE is fully on Pt-Gd alloys.

**Gd electrodeposition.** Two approaches for the electrodeposition of Gd were pursued, the deposition from an ionic liquid with TFSI anion at room temperature, which was based on prior experiments with La, and the electrodeposition from another ionic liquid at elevated temperatures.

In order to study the general electrochemistry of precursor solutions, studies using cyclic voltammetry at slow scan rates were carried out in combination with EQCM. Based on those results, conditions for potentiostatic and pulse plating attempts were selected. Cyclic voltammograms together with the frequency and damping change recorded at a scan rate of 10 mV/s are shown in Figure 14. In the cyclic voltammogram recorded in the potential range down to -2.5 V (14a) one cathodic peak can be observed at around -1.3 V and an increase in current at about -2.3 V. However, the total current magnitude was still very low. The EQCM resonance frequency and damping change therefore did not show a unique trend that could be correlated with a deposition process. However, when the potential range was extended further to -3.5 V, the situation changed. Below -2.8 V, both resonance frequency and damping decreased, the former therefore being indicative of a deposition process. At even lower potentials, electrolyte decomposition occurred and a coupled frequency-damping change was observed (14b). Thus there was indication for deposition in this electrolyte, but not as clear and well separated from the electrolyte decomposition region as in more ideally behaving electrolyte systems.

![Figure 14](image)

**Figure 14.** Cyclic voltammograms recorded at room temperature from a TFSI based IL (black lines) together with frequency (red lines) and damping (green lines) changes.

Based on these experiments, potentiostatic deposition experiments were carried out. In Figure 15, a current transient measured is shown together with the corresponding frequency and damping changes. In the very beginning, there is a strong current decrease and a rather gradual decrease in the resonance frequency, corresponding to a very slow electrodeposition process. After ~10 min, however, the current starts to increase and at the same time there is a much larger frequency change. This indicates that the deposition process has an induction phase. A possible explanation might be the presence of strong interfacial layers that have been observed in literature\(^{12,13}\). For a pure Gd electrodeposition process from Gd(III), one would expect a value for the ratio between deposited mass \(dm\) and transferred charge
\[
\frac{\mathrm{d}Q}{\mathrm{d}Q} = -\frac{M}{3F} = -5.43 \cdot 10^{-4} \text{ g/C}.
\]

Within the induction period, a value of \(-1.9 \cdot 10^{-4} \text{ g/C}\) was obtained, while afterwards a value of \(-6.9 \cdot 10^{-4} \text{ g/C}\) was seen. Mass changes were estimated from Sauerbrey’s equation \(^{14}\). However, the application of this equation is not really justified, as the damping change is of a similar magnitude as the change in \(\Delta f\). Therefore the fact that a value larger than expected is obtained is not surprising. Several results were obtained strongly pointing towards Gd metal deposition but at relatively slow kinetics.

\[\text{Figure 15. Current transient (black line) for Gd deposition together with corresponding frequency (red line) and damping (green line) change recorded in a TFSI based IL.}\]

Besides potentiostatic plating at a constant potential, pulse plating was studied as well. In pulse plating deposition at a suitable potential is interrupted for a certain time to permit diffusion of reactants to the surface. Thus a continuous depletion of reactant at the interface shall be avoided. The potentials both for deposition (“ON”) and no deposition (“OFF”) and the corresponding pulse lengths need to be chosen carefully. Several sets of experiments with different potentials and different ON/OFF times were carried out. Conditions suitable for deposition were identified (cf. Figure 16).

\[\text{Figure 16. Potential (green line), frequency (black line) and damping (red line) change recorded during pulse plating of Gd in a TFSI based IL.}\]
The second approach is based on the electrodeposition of Gd from another IL using a different Gd precursor. This ionic liquid could not be used at room temperature. At elevated temperatures, however, electrochemical measurements could be carried out. After voltammetric studies, conditions for potentiostatic and pulse plating were identified, that permitted the deposition of thick layers of Gd metal. A typical cyclic voltammogram is depicted in Figure 17a. A pulse measurement is shown in Figure 17b.

![Cyclic voltammogram at 5 mV/s and frequency and damping change recorded in an IL based Gd electrolyte](image1)

![Current transient (black line), frequency (blue line) and damping (red line) change recorded during pulsed Gd electrodeposition.](image2)

A rather thick deposit on the electrode was obtained, as shown in Figure 18. The deposit, taken out from the glovebox immediately after deposition was grey in color indicating metal deposition. After washing with isopropanol a white discoloration was observed, indicating oxide formation.

![Images of the obtained deposit a) immediately after deposition and removal from glovebox and b) after washing with isopropanol.](image3)
The deposition of Gd could be repeatedly and reliably obtained from this electrolyte. Therefore also the deposition of Pt and of a Pt-Gd alloy were attempted. However, at least in the potential range studied, with the chosen Pt precursor there was no evidence for Pt deposition. Also from mixed Pt-Gd electrolytes no deposition was obtained. Therefore Pt deposition and alloy formation need to be further studied.

2.4. **Task 3.5. Hybrid non-PGM/@Pt catalysts with ultralow Pt loading**

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**CNRS contribution**

For a long time, platinum-based catalysts have been the only candidates for the cathode of polymer electrolyte fuel cells (PEMFCs)\(^\text{41}\). This will result in a huge economic challenge if such fuel cells are to be mass-produced in the future. More recently, several breakthroughs have occurred in the field of non-precious group metal non-PGM FeNC-catalysts, making them worthy competitors to platinum.\(^\text{41-44}\) However, before these FeNC catalysts can be introduced as commercial polymer electrolyte fuel cells, their durability in real PEMFC condition must be greatly addressed and improved compared to the current state.\(^\text{44}\)

Increasing the active site density is a key point in ORR activity of FeNC catalysts. Increasing the starting precursor of the metal, typically, iron, does not necessarily result in higher active site density. Usually, the extra iron content form unwanted Fe species which are not only ORR inactive but also block the other active sites and prevent substrate diffusion. Therefore, in many works reported before, there is an additional step such as acid leaching which removes these moieties from the catalyst surface.\(^\text{44}\)

Therefore, presenting a solution which improves the incorporation of metal inside the carbon structure which means increasing the active site density is an important issue. While high temperature pyrolysis of any mixture of carbon, nitrogen and metal (Fe, Co, Ni, Mn) precursors result in an ORR active catalyst, the final activity and stability largely depend on the rational choose of the starting precursors. We previously reported the most active Pt-free FeNC catalysts prepared from phenanthroline, Fe\(^{II}\)-acetate, and the metal organic framework ZIF-8. We also showed that the crystal size of ZIF-8, the starting metal content and the synthesis conditions should be optimised to achieve the highest performance.\(^\text{45}\) However, most of these investigations only addressed the activity of the final material and achieving long term stability was not addressed. Our recent results showed that trace amounts of H\(_2\)O\(_2\), an ORR by-product, significantly damage these catalysts.\(^\text{46}\) Due to the high activity of metallic Pt toward H\(_2\)O\(_2\) reduction, we hypothesised that addition of minute Pt can improve the stability of the catalysts.\(^\text{47-48}\) In previous studies on Pt/FeNC hybrid catalysts, the crucial role of Pt was increasing the final activity. In contrast to the previously published works, here we assessed the effect of minute Pt NPs on the stability of the Pt/FeNC cathodes. Accordingly, we selected our most active FeNC catalysts derived from ZIF-8 and impregnate it with Pt salt to investigate the stabilisation effect of Pt on FeNC. Physical characterisations, in particular Mössbauer and XPS, paved the way to correlate the final performance and composition/structure of the materials.
**Synthesis of Pt/Fe-NC Catalyst:** All the Fe-based non-precious metal catalysts, Fe-N-C, were prepared via the dry ball-milling of Fe(II) acetate (Ac), 1,10-phenantroline and (ZnN₄C₆H₁₂, Basolite Z1200 from BASF, labelled ZIF-8). For a typical synthesis, corresponding to 1 wt% Fe in the catalyst precursor before pyrolysis, 32.45 mg Fe(II) Ac, 200 mg of 1,10-phenanthroline and 800 mg of ZIF-8 were weighted and poured into a ZrO₂ jar (Figure 19 step 1). Thereafter, 100 zirconium-oxide balls with 5 mm diameter were added, the jar closed under air and installed in the planetary ball. The starting precursors were milled for 2 hours in total at a speed of 400 rpm, applying 4 cycles of 30 min. The mixing process in the ball miller was followed by a pyrolysis step at 1050 °C under Ar for 1h via flash heating procedure (Fe content in the catalyst is ca 3 wt % due to 66-70 wt% mass loss from ZIF-8 and phen during pyrolysis). The quartz tube was removed after the dwelling time and left to reach the ambient temperature under Ar atmosphere. The Fe-N-C catalyst was collected from the oven at room temperature.

**FeNCsynthesis**

**impregnation of FeNC by Pt salt**

**Synthesis of Hybrid Pt/Fe-NC Catalysts:**
Three methods were developed for synthesis of hybrid catalysts:
**Thermal Reduction (TR):** The FeNC catalyst was impregnated by drop wise addition of Pt salt. After drying the sample under air at 80 °C, the samples were thermally reduced under 5 different reducing conditions in oven at high temperature. The samples were labelled as x-TR-y.
**Chemical Reduction (CR):** The Pt precursor was added to FeNC in the presence of a reducing agent. The reduction condition was controlled in two different pHs for two different Pt salts. These samples were labelled as x-CR-y.
Physically Mixed Hybrid (PMH): The Pt nanoparticle were synthesised separately and deposited on the final FeNC catalysts. These samples were labelled as x-PMH-y samples.

The following techniques were applied to characterise the Fe-N active sites and Pt nanoparticles: Mössbauer measurements were performed to characterise the nature of the iron oxidation state and coordination environment within catalyst structure. XPS was used to probe the Pt oxidation state. Rotating disc electrode (RDE) and fuel cell tests were applied for electrochemical characterisation of final hybrid catalysts.

Activity and stability of hybrid Pt/FeNC catalyst variants: We previously showed that minute amounts of platinum NPs can stabilise Fe-N-C catalysts in PEMFC. These Pt/Fe-N-C hybrid catalysts were prepared by wet impregnation of Fe-N-C (1 wt% Fe in the initial precursor) by a Pt salt and its post-thermal treatment. These results are summarised in Figure 20.

![Figure 20. a) Chronoamperometry (CA) of FeNC and Pt/FeNC hybrid catalysts. The stability tests were performed at 0.5 V for 50h. b) mass activity at 0.8 V before and after CA tests.](image)

Accordingly, while the H₂-Fe-N-C catalyst (Pt-free Fe-N-C catalyst) partially lost its initial activity during the 50 h test, addition of Pt NPs did not increase the initial ORR activity but stabilised 1-TR-1 and 2-TR-2 catalysts during FC operation. Based on these previous results, the influence of other reducing conditions on ORR activity and ability to stabilise Fe-N-C was investigated. Accordingly, the mass activity of X-TR-Y was determined in MEAs in single fuel cell operation.

Figure 21 summarises the mass activity of the catalysts at 0.8 V in PEMFC for different Fe-N-C and hybrid catalysts. It was necessary to first optimise the Fe content in Fe-N-C. This is shown in the first set of columns of Figure 21. By increasing the Fe content from 1 to 2 or 4 wt% (content before pyrolysis), the mass activity levels off or even decreases. Fe₁₇wtt%-NC was therefore chosen for the synthesis of hybrid catalysts in this work. The second and third set of columns show how the ORR mass activity abruptly increases for Pt/Fe-N-C hybrid catalysts for 2-TR-4 and 2-TR-5, relative to those treated in other reducing conditions. As expected for ORR-active Pt NPs, the 2-TR series samples showed higher mass activity than that to 1-TR.
In Figure 21, the mass activity of the chemically reduced Pt/Fe-N-C hybrid catalysts are compared to that of the thermally reduced and physically mixed hybrid samples. Chemical reduction was carried out at two different pHs, and two different Pt salts were investigated, leading to four different Pt/Fe-N-C hybrid catalysts obtained by chemical reduction of the Pt salts. These samples are labelled 2-CR-y, y referring to reducing pH and Pt salt. All of these four samples show lower activity than 2-TR-5 and also lower or equal activity to that of the reference 2-TR-1 which was reduced in milder conditions. The sample 2-CR-4 shows highest activity of the CR samples.

![Figure 21. Initial mass activity in PEMFC of Fe-N-C and Pt/Fe-N-C catalysts at 0.8 V.](image)

Figure 22 compares the initial and final mass activities of the most active sample of each series of Pt/Fe-N-C hybrids after 50 h voltage hold at 0.5 V. Most of the hybrid Pt/Fe-N-C materials (except that prepared by chemical reduction of one salt) are stable over this 50 h period. In contrast, the Pt-free samples show significant ORR activity loss over 50 h (activity loss by a factor of 3). This shows that Pt, independently of the synthesis method, stabilises Fe-N-C in the hybrid catalysts.
The iron speciation, a key to the intrinsic activity of Fe-based catalysts, was investigated by $^{57}\text{Fe}$ Mössbauer spectroscopy. The results are depicted in Figure 23 for typical samples, 2-TR-1 and 2-TR-5. The spectra of Fe-N-C and all Pt/Fe-N-C reveal a sextet and a singlet assigned to α-iron, and two quadrupole doublets D1 and D2. The latter are Fe$_x$N$_4$C$_x$ moieties in low and medium spin states, which are considered as the most active sites in Fe-N-C catalysts, while γ-Fe and α-Fe are less active or inactive species towards ORR. The results show that increasing the Fe content in the starting precursor increases the relative content of γ-Fe and α-Fe, which explains the lower activity in 2 wt% Fe-N-C compared to 1 wt% Fe-N-C (Figure 23 a-b). The thermal reduction and presence of Pt do not result in a significant change in the $^{57}\text{Fe}$ Mössbauer spectra. In particular, no further formation of metallic Fe or Fe$_x$C species was detected. The isomer shift and quadrupole splitting of D1 and D2 are similar in the reference Fe-N-C catalysts and in the Pt/Fe-N-C hybrid catalysts, demonstrating that the same ORR active FeNx sites are present in both cases.
For the synthesis of 2 wt% Pt/C catalyst the carbon was slurried in weakly basic water before addition of the metal salt. On complete deposition of the metal, the metal was reduced either by chemical methods or by heat treatment under reducing atmosphere at different temperatures. The catalyst powder was then washed in water until the conductivity of the leachate was below 10 S. The catalyst was characterised by XRD analysis with a Bruker AXS D-500 Diffractometer and XRD crystallite sizes determined for each catalyst. The catalyst metal surface area was determined from gas phase chemisorption with carbon monoxide.

A 2% Pt/C catalyst was made at JM following the procedure described above and characterisation data is shown in Table 5.

**Table 5. Details of the 2% Pt/C JM catalyst.**

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>Pt assay / %</th>
<th>Metal area / (m²/g Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG5074</td>
<td>1.97</td>
<td>121.83</td>
</tr>
</tbody>
</table>
2.5. Task 3.6. Feasibility of catalyst layer development

**JM contribution**

Measuring initial activity and stability of new catalyst formulations in pure oxygen is the first step towards the discovery of new catalysts for the oxygen reduction reaction (ORR). However, it is essential to integrate new catalyst formulations into catalyst layers that can deliver the highest performance in a fuel cell. This is a laborious task where different steps and components must be tuned with care. In essence, a good catalyst layer needs to deliver optimum transport for gas and liquid under a wide range of humidities, pressures and temperatures. This is particularly challenging because a small change in the operating conditions can lead to a significant change in performance and in some cases the benefits identified with a new catalyst formulation in pure oxygen can be lost, due to a poor catalyst layer configuration, when tested in a fuel cell under H₂/Air. Therefore, in this task, efforts have been directed towards the successful integration of catalyst formulations, so far developed in Task 3.4, which have met activity and durability criteria under H₂/O₂ and H₂/Air. The ultimate aim of this task is to integrate catalyst formulations into catalyst layers and assess initial performance in single fuel cells under a wide range of operating conditions. The catalyst layers that show good performance can then be transferred to WP4 for further tuning and refinement for larger scale hardware.

**MEA preparation:** A membrane electrode assembly consists of anode and cathode catalyst layers (or electrodes), anode and cathode gas diffusion layers (also referred to as GDLs), and a proton-conducting membrane. Therefore, the MEAs used in this work consisted of five layers. Nafion 1100 EW (equivalent weight in g polymer/mol H⁺) aqueous ionomer perfluorosulphonic acid (PFSA) was used to fabricate thin-layer electrodes. The cathode catalyst layers were prepared at ionomer/carbon weight ratios ca. 0.8/1 and metal loadings ca 0.2 mg Pt/cm², unless specified otherwise. The anode catalyst layer was kept constant at an ionomer/carbon weight ratio ca. 1.5/1 and a metal loading of 0.1 mg Pt/cm². The membrane used in this protocol was a PFSA type, made at JM with a thickness ca. 20 µm.

Catalysts layers were deposited onto a PTFE release substrate and then transferred via a decal method onto the membrane. The decal transfer process consisted of hot-pressing the 50 cm² catalyst-coated PTFE sheets onto the polymer electrolyte membrane. Uniformity in pressure distribution during decal transfer was obtained by using suitable pressure distribution pads. After fabrication, the active area on each electrode was reduced to 6 cm², (3x2) cm, with the lamination of a ‘picture frame’ seal over the electrode area. Commercially available gas-diffusion layers (GDLs), based on fluoro-polymer treated carbon fibre paper substrates, were used for this work and were adjusted to optimise gas and water transport at the anode and cathode electrodes. Single cells (6 cm² active area) were assembled by sandwiching the catalyst coated membranes (CCMs) between the appropriate GDLs and applying a suitable compression onto the active area.

**Fuel cell testing:** The fuel cell station used was built in-house at JM. Pure oxygen and synthetic air were used as cathode reactants and pure H₂ as the anode reactant (all gases of 99.9% purity). Stoichiometric flow rates of anode (s = 2) and cathode (s = 9.5 for O₂ and s = 2 for air) reactants were used at current densities >0.2 A/cm² and constant flows (corresponding to 0.2 A/cm² flows) were used at <0.2 A/cm². Reactant humidification was achieved by water-bubblers, the temperatures of which were calibrated to
yield the quoted relative humidity (RH) values. The humidity and cell pressure was measured at the
inlets for the anode and cathode. Cell resistances as a function of current density (i.e. the sum of the
proton-conduction resistance in the membrane and the various electronic resistances (bulk and contact
resistances)) were determined using an AC perturbation of 1 kHz at three different current densities of
25, 50 and 100 mA/cm² and by using a current interrupt method. For each data point, the cell voltage
was stabilised over 10 minutes and data was averaged over the last minute. Multiple-path serpentine
flow-fields (two and three parallel channels for the anode and cathode, respectively) machined into
sealed graphite blocks were used for testing.

The MEAs were conditioned by the application of a constant current density of 500 mA/cm² under
H₂/Air at 50 kPa gauge, 100% RH and 80 °C. The cell voltage was monitored until a stable value was
observed. The conditioning step lasted 2h unless specified otherwise. The test protocol used was
described in detail in Deliverable D3.1, with the exception that in this case the cell temperature and
pressure were varied to cover a wide range of operating conditions and these are described in detail in
the text.

The current distribution measurements were made using a current scan shunt unit (S++) in a 50 cm²
housing in a liquid cooled fuel cell hardware (qCF50 Baltic Fuel Cells) connected to the standard fuel cell
test station. Measurements were made every 10 s during the protocols described above with the
analysis and visualisation carried out using a combination of in-house scripts and ParaView (Kitware).

From the work described in Task 3.4, catalysts F and G, Table 2, were identified as candidates for further
optimization in Tasks 3.6. Figure 24 shows the performance of catalyst G with two different catalyst
layer configurations shown with the red (layer 1) and blue (layer 2) dashed lines, and compared to the
Pt/C benchmark catalyst layer in WP3, green line. The two catalyst layers have been tuned with different
components in order to observe the behavior of these catalysts layers at low and high current densities.
From Figure 24 it can be seen that the two catalyst layers with catalyst G perform very similarly under
H₂/O₂ and show a 20mV increase in performance vs the benchmark catalyst (A) at all current densities.
However, under H₂/Air the two catalyst layers perform similarly up to 1.0 A/cm² but catalyst layer 1 (red
line) clearly shows high mass transport losses at higher current densities. On the other hand, catalyst G
used in catalyst configuration 2 (blue line) shows much better performance at higher current densities
compared to configuration 1.

Performance of catalyst G, as layer configuration 2 (blue line), performs within 10% of the benchmark
catalyst layer under H₂/Air and this catalyst layer therefore meets the project Milestone 1 requirements
under these conditions.
In order to understand the limitations of these catalyst layers at high current density (such as layer 1 in Figure 24), we performed current mapping during operation. Current mapping offers an excellent tool to identify differences between catalyst layers during operation and can show, in real time, differences in current distribution which can be attributed to differences in the catalyst layer. Similar observations were obtained for PtNi catalyst F and some of the results are shown at the end of this section.

Figure 25 shows a current map of catalyst layers at 1.5 A/cm², with a dealloyed PtNi/C (Catalyst G, layer 1) compared to the WP3 benchmark catalyst layer.

Results show that the catalyst layer with the alloy catalyst G, layer 1, suffers from a non-uniform current distribution compared to the benchmark catalyst layer at the high current density of 1.5 A/cm². The area with lower current is highlighted with a red circle in Figure 25 as a guide to the eye. Similar observations were obtained at different humidities but were less pronounced at lower RHs. Our current...
hypothesis is that this catalyst layer is not capable of eliminating water fast enough to allow optimum oxygen transport to the catalyst surface. This is exacerbated on the bottom half of the cell where the oxygen concentration is lower than in the upper half, due to pressure drop and consumption effects down the cell. This leads to some areas not being well utilised, as shown in Figure 25, and therefore as the current density increases the overall performance (voltage) of the catalyst layer decreases quite significantly.

An additional diagnostic test was carried out with the use of AC impedance. This test was used to measure proton conductivity in the layer and membrane resistance, among other parameters. Overall results showed that the catalyst layer proton conductivity was lower with the use of dealloyed PtNi catalysts (F & G) compared to the benchmark catalyst layer (A). This was attributed to the leaching of nickel ions into the ionomer and the membrane. Experimental evidence was obtained with the use of electron probe micro-analysis (EPMA) cross section analysis before and after durability testing and in all cases we obtained evidence of nickel ion migration into the membrane. To improve further the performance of these dealloyed catalysts more catalyst development iterations will be conducted in Task 3.4.

In order to validate further the good performance of PtNi catalysts F and G, the best catalyst layers were tested under a wide range of temperature and humidity and results are shown in Figure 26. This test offers a good screening tool that identifies the performance of a catalyst layer under conditions that are relevant to the automotive fuel cell stack operation. In essence, Figure 26 extends the performance shown in Figure 1 but to a wide range of RHs and temperatures.

For simplicity, Figure 26 shows the cell voltage (not iR corrected) at a high current density of 1.6 A/cm² at different cell relative humidities (RHs) and temperatures.

Figure 26. Measured cell voltage at 1.6 A/cm² at different cell humidity and temperature at 100 kPaₑ⁻inlet. Black line shows performance of benchmark catalyst layer (A) compared to the new Pt/C catalyst C (red line), PtNi alloy catalysts F (blue line) and G-layer 2, from Figure 1 (green line).
Results in Figure 26 show that both PtNi catalysts F and G perform within 10% of the benchmark catalyst layer under dry and wet conditions and at high current density. In addition, the new Pt/C catalyst (C-red line) also performs well, in particular under dry RH compared to the benchmark WP3 catalyst layer (A).

This is a remarkable result and in this task catalyst G, as layer configuration 2, which was transferred from Task 3.4, has been successfully incorporated into a catalyst layer in Task 3.6 and meets the project Milestone 1 under a wide range of operating conditions. Catalyst F, although it does meet the high current density performance target in H₂/Air and shows very good performance across a wide range of operating conditions, did not meet 2xPt mass activity defined in Task 3.4. However, there is room for improvement with this formulation to increase the mass activity in future work. Lastly, the new synthesis route for Pt/C has demonstrated a clear benefit under dry conditions, compared to the benchmark catalyst and this is a further significant achievement in Task 3.6.
3. SUMMARY AND CONCLUSIONS

With regard to Task 3.2, VTT has focused on development of fibrous carbon support materials as well as improved tie-layers. Inclusion of CNTs into PAN precursor solutions resulted in reduction of fibre diameters and pressure and/or solvent treatment seem feasible methods for densifying carbon fibre support networks. Multivariable study is ongoing for a better understanding of the optimal composition and recipe for Ti-Nb oxide tie-layers, however, characterisation has proved challenging and, thus, work is still ongoing. VTT has also built capabilities for particle ALD, so when optimal tie-layer is determined, we can produce corrosion resistant carbon support materials ranging from particles to fibrous supports with smaller fibre diameters and/or densified structure. VTT support development work and tie-layer optimisation has progressed as expected. Work is still ongoing, but when the tie-layer study, and thus better understanding of the optimal Ti-Nb-oxide tie-layer configuration is obtained, we will be able to produce corrosion resistant supports firstly based on sub-µm to nano-scale fibrous carbon webs with smaller fibre diameters, denser and thus thinner structures than previously, and secondly using commercial carbon particles.

JM focused its activities on the synthesis and characterisation of modified carbon supports via ALD with tie-layers and two such carbon supports were received from two external companies, with different metal oxide loadings. Different annealing steps were studied in order to gain better understanding of the impact on conductivity of the carbon supports after modification. Out of this work, one modified carbon support was identified as a suitable candidate to transfer to Task 3.3 for Pt catalysation via ALD or by chemical methods. In addition, wet chemical methods were explored as routes to deposit transition metals and then form doped carbon supports. This was successfully achieved and five different TM-carbon supports were identified as suitable candidates to transfer to Task 3.3 for Pt addition via wet chemical methods.

In Task 3.3, a new, fast and scalable process was developed at CNRS for the synthesis of nickel-platinum core shell nanofibres; all the catalysts produced using the microwave assisted galvanic exchange demonstrated properties above the INSPIRE target for mass activity both at the beginning of testing and the end of testing (Figure 27). The ECSA, specific activity and mass activity values were obtained from characterising these catalysts ex-situ in a three electrode cell, adopting the INSPIRE characterisation protocol.

The general trend observed is that lower platinum loading (< 10 wt%) results in higher activity, but lower stability, whilst higher platinum loading results in a catalyst with outstanding stability but still showing mass activities above the project target.
A first protocol aimed at reducing the nickel dissolution during operation was developed but resulted in reduced performance bringing the key figure for ex-situ catalyst assessment, the mass activity, below target.

CNRS has developed a new morphology for the self-standing electrodes that could remove the drawback observed during the earlier implementation of electrospun carbon nanofibre self-standing electrodes in MEAs. This new process allows control and tuning of the lacunarity of the electrodes, as well as the density and surface area along the thickness of the electrode. Furthermore, the presence of nanotubes not aligned to planes parallel to the electrodes should reduce the anisotropy of the connectivity, thus promoting more efficient proton transport within the catalyst layer.

A modified carbon support with a tie-layer, made via ALD, transferred from Task 3.2, has been successfully catalysed at JM with Pt, via ALD and wet chemical methods. In the case of the ALD Pt addition, a range of deposition cycles had to be explored, until a stable and uniform dispersion was obtained. The measured surface areas in the cell were in line with the wet chemical methods and this gives confidence that the ALD route can produce good catalyst dispersions on to the tie-layer coated carbon support. Ex-situ, gas-phase metal areas were much higher however, and this discrepancy needs to be resolved; it may indicate a potential benefit of the ALD catalysation. Unfortunately, the electrochemical testing revealed lower performance of the ALD Pt catalyst and lower stability compared to the benchmark catalyst. In close collaboration with VTT, work has been also conducted with the aim of gaining better understanding of the interaction between Pt and the TiOx layer with the use of coated silicon wafers. From this work we aim to improve the morphology and stability of the ALD Pt catalysts on to the modified support. Overall, this route is giving very promising catalysts and work will continue with the synthesis of modified supports with higher conductivity and optimisation of ALD deposition, in order to improve the Pt dispersion.

In Task 3.4, reduced-size PtNi and PtNiMo alloy octahedral nanoparticle catalysts were successfully synthesised at TUB. The small size, ~ 7 nm, allows for good values of the ECSA for octahedral Pt alloy
nanoparticles catalysts. Improvements in the catalyst morphology and dispersion might further increase the ECSA, which is still below 50 m²g⁻¹Pt. High initial mass activity is observed, which remains well above the activity target even after a small degradation observed during the stability test. The Mo surface doping process increases the mass activity even further, with the best samples showing an initial mass activity of 3.7 A/mgPt. Based on these results, the Mo doped PtNi/C shows promises for testing in membrane electrode assemblies (MEAs). The amount of catalyst produced is currently being scaled up to be able to reach values of grams, necessary for the MEA testing.

At JM, a matrix of over 20 catalyst variants was created using three different synthesis routes that produced PtNi catalysts on two different carbon supports. The catalysts were incorporated into cathode catalyst layers and evaluated as MEAs in single cells for stability and high current density performance. All the PtNi formulations had kinetic mass activities higher than the benchmark catalyst (A), and some of them also exceeded 0.44 A/mgPt. After a voltage cycling AST the PtNi catalyst layers also retained more Pt surface area and mass activity compared to the WP3 benchmark catalyst layer. However only PtNi alloy catalysts F & G exceeded the performance of the WP3 benchmark catalyst layer and catalyst F improved on the benchmark catalyst layer at high current density (1.5 A/cm) on H₂/Air. From the work in this task, alloy catalysts F & G, in addition to Pt/C catalyst C, progressed to further layer optimisation in Task 3.6 and the results are shown in this report. In addition, the Pt addition to modified carbon supports with transition metals has shown promising results for one of the formulations explored. Further work is planned in order to validate the full benefits of this approach and, if successful, these modified supports will be catalysed with the most active PtNi alloy formulations identified in Task 3.4.

At TUM, two approaches were used for the deposition of Gd, based on potentiostatic and pulsed plating from two different electrolytes, one at room temperature and one at elevated temperatures. The deposition at room temperature was very sluggish, probably due to the presence of the interfacial layers impeding metal deposition. Pulse plating alone as an optimisation trial was insufficient for Gd deposition working at room temperature from the TFSI based electrolyte. Potentiostatic deposition for a longer time and polarization to very negative potentials, however, facilitated the deposition. Gd deposition was accomplished readily from a second electrolyte at elevated temperatures, with deposition of large amounts of material in short time. First attempts to deposit Pt from this ionic liquid failed, but should eventually work. As no alloys have been prepared yet, information on mass and current activities cannot be provided.

In summary for Task 3.4, new catalysts with improved stability and activity with respect to the benchmark catalyst were successfully prepared following several different approaches and are progressing towards further layer optimisation in Task 3.6. These include a highly active ~ 7 nm reduced-size PtNiMo alloy octahedral nanoparticle catalyst on carbon support, as well as formulations of dealloyed PtNi on different carbon supports and a new Pt/C catalyst. Furthermore, the Pt addition to modified carbon supports with transition metals has shown promising results for one of the formulations explored. Finally, a promising approach to synthesise a PtGd alloy catalyst is under investigation. Gd deposition was accomplished readily from an optimised electrolyte at elevated temperatures, with deposition of large amounts of material in short time, while deposition of Pt from this IL is currently under investigation.

In Task 3.5, CNRS showed that functionalisation of FeNC catalysts by very small amounts (0.5-2wt%) of Pt increases the stability of Pt/FeNC hybrid catalysts. The starting Pt precursor (initial Pt oxidation state) and method of synthesis of Pt nanoparticles play crucial roles in final catalyst performance. The most
active samples are synthesised by wet impregnation followed by thermal reduction with more active catalysts prepared in an increasingly reducing environment. XPS analysis of the samples showed that > 50% of the Pt detected by XPS is oxidised (Pt$^{2+}$ and Pt$^{4+}$) and that for a given preparation route, catalysts with higher mass activity have a higher fraction of Pt$^{0}$. The use of nano-ZIFs increases the activity of FeNC catalysts beyond what is observed using commercial ZIF-8.

In Task 3.6, two dealloyed catalysts (F & G) transferred from Task 3.4 were integrated into catalyst layers. A series of different ionomers, ink types and layer properties were studied in order to find out the formulations for best performance. Catalyst G had a particularly unusual interaction with the ionomer and in some cases its performance at high current density under H$_2$/Air suffered from high mass transport losses. With the use of current mapping it was identified that at high current densities, the current distribution was not uniform across the catalyst layer. In addition, the layer proton conductivity for catalysts F & G was lower compared to the benchmark catalyst A. These two differences, in addition to the intrinsic differences in catalyst layer structure compared to the benchmark catalyst, were responsible for the decrease in performance at high current densities. After several iterations, catalyst G was integrated into a different catalyst layer configuration with a significant increase in performance. The work in this Task 3.6 has demonstrated that MEAs with two new cathode layers (using catalysts F & G) also exceeded the performance of the WP3 benchmark catalyst layer at high current density (1.5 A/cm$^2$) on H$_2$/Air by at least 7%, under a wide range of operating conditions.

Catalyst G in layer 2, meets the project Milestone 1 and therefore it will be transferred to WP4 for further optimisation. Catalysts C and F will also be offered to WP4.

The overall progress in WP3 at M15 allows us to highlight the promise of PtNi formulations as thin films (Task 3.3, CNRS), shaped particles (Task 3.4, TUB) and dealloyed catalysts (Task 3.4, JM) that reach the project mass activity and stability targets. Preparation of other alloy formulations, in particular GdPt, have encountered experimental challenges but are nevertheless progressing and mass activity and stability data will be reported subsequently. Work in Task 3.4 on dealloyed PtNi catalysts moved forward to such an extent that the feasibility of catalyst layer development and scale-up were initiated earlier than planned, with positive results, which is an important outcome for WP3 in the context of the requirement to deliver a scaled-up catalyst for validation in the GEN2 stack design at Month 18.
4. Recommendations and Future Work

Task 3.2

Further work on understanding the conductivity of the modified carbon supports needs to be done during the annealing step. This is crucial in order to identify a modified carbon support with higher conductivity and therefore reduce losses during operation in a fuel cell, in particular at high current densities. Therefore, in-situ analytical techniques will be explored such as in-situ XRD and in-situ TEM with a heating stage under controlled atmospheres, among others, to probe the crystal structure and morphology of the oxide tie-layers. In addition, routes capable of producing carbide modified supports with transition metals at lower temperature will be explored.

Task 3.3

PtNi nanowires: A novel stabilisation protocol for a nickel-platinum core shell nanofibrous catalyst has been recently reported and an evaluation of its applicability to the microwave synthesised catalyst should be performed. Ex-situ data shows that these catalysts have the potential to bring MEA performance above the project target; nevertheless, their morphology is new and there is no previous literature on MEA performance of nickel platinum core shell nanofibers, therefore how well the ex-situ characterisation will match the properties of an MEA prepared using this catalyst is unknown. Similarly, the extent of nickel leaching during actual MEA operation and its effect is still unknown. Therefore MEA preparation and evaluation are the next key steps to perform. Based on the results shown, we have down-selected the 25 %wt platinum loading core shell catalyst as the first for MEA testing; the mass activity and stability of this catalyst are more than promising, although a small concern is raised by the ECSA value below 50 m²/g that could result in poor performance at high current densities.

Pt thin films on nanofibers: A wide range of synthesis approaches have been explored in Task 3.3. As a result it was possible to produce a library of nanofibres with different morphology, fibre density and composition. Attempts were made to coat these fibres with Pt via electrodeposition. A first set of platinised hierarchical CNF-CNT electrodes has been prepared and initial characterisation results show experimental evidence of successful Pt addition. These interesting materials will progress to electrochemical evaluation in wet cells and in single fuel cells.

ALD-Pt / TiOx-C catalysts: The use of ALD as a tool to modify commercial carbon black supports has shown to be a very promising route towards the synthesis of more corrosion resistant supports. Within this area we need to gain better understanding of the mechanisms that control the conductivity of the modified carbon supports with doped tie-layers. This is a laborious task but essential to identify novel supports that can lead to high stability and hence help to meet the ultimate project performance and durability targets. Future work will focus on the synthesis of modified carbon supports via ALD and the subsequent catalysation with platinum or platinum alloy catalysts.

Task 3.4

Shaped particle catalysts: Future work aims to improve the morphology in terms of yield of octahedral, with respect to cubo-octahedral particles, and to reduce agglomerates. In addition we will aim at further improving the performance and stability by finely tuning metal compositions and investigating modifications of the surface doping process.
**Dealloyed PtNi particle catalysts:** Further work will be focused towards the synthesis of dealloyed catalysts with higher surface area, which is thought to be key to meet performance at high current densities. In addition, new chemistries still need to be explored in Task 3.4 that allows the synthesis of more stable alloy catalysts. This is because nickel dissolution is still seen as the primary cause of performance loss during operation. In addition, it is planned to explore to use of a corrosion tolerant carbon support with the most active alloy formulations identified in this task. Addressing these properties is key to reach the ultimate project performance target of 1.5 W/cm$^2$.

**GdPt alloy catalysts:** The major next step will be the deposition of Pt metal using other precursors. Gd deposition will be repeated also with a true reference electrode. This will permit determination of the best parameters for alloy deposition. After successful alloy deposition as bulk film and testing of its electrocatalytic behavior, nanoparticles will be produced.

**Task 3.5**

**Pt/FeNC catalysts:** The nature of the Pt precursor, ZIF-8 particle size, catalyst reduction process conditions as well as other experimental parameters all influence the final Pt/FeNC catalyst mass activity and performance/durability as investigated in membrane electrode assemblies. The next step is to combine the precursors and process conditions that have given the most prospective results, to continue to improve catalyst activity and stability.

**Task 3.6**

**Catalyst layer formulations:** Further work will be focused towards the optimisation of new catalyst layer formulations that meet the criteria defined in Task 3.6. Particular emphasis will be given to catalyst layer characterisation, in order to gain a better understanding of the interaction between the ionomer, the catalyst and the support. The use of cell diagnostics, such as current mapping and AC impedance will also be extended, in order to identify the reasons for the increase or decrease in performance of catalyst layers compared to the benchmark. Addressing these properties is key in order to reach the ultimate project target of 1.5 W/cm$^2$.
5. References

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