CATAPULT

NOVEL CATALYST STRUCTURES EMPLOYING PT AT ULTRA LOW AND ZERO LOADINGS FOR AUTOMOTIVE MEAS

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DELIVERABLE REPORT

D4.4 – DEMONSTRATION OF PT-CATALYSED NON-CARBON SUPPORT WITH HIGHER MASS ACTIVITY THAN CONVENTIONAL PT/C NANOPARTICLES AND IN EXCESS OF 0.15 A/MG PT	
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NATURE OF THE DELIVERABLE		
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P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY	
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Abstract	

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1   Introduction

The key objective of Work Package 4 is to achieve a platinum utilisation of <0.1 g Pt/kW at useful power densities at the end of the life of an MEA. The logic behind the mass activity target of this report and the associated milestone, Milestone 2, is that an acceptable mass activity should be achieved in order to give the subsequent catalyst layer optimisation a realistic chance of achieving the desired power output. The performance of the catalyst and MEA at the high potential used to characterise mass activity (0.9 V) is actually of very little practical importance; rather it is a fingerprint of a suitable catalyst, but no more.

The other key requirement is that the high performance should be achieved using a support that is corrosion resistant. Whilst it is still the current fuel cell catalyst support of choice, carbon is considered to not have the corrosion resistance under realistic operating conditions necessary to give an end of life performance good enough to facilitate mass market adoption of fuel cells for automotive applications. This is why the target for this deliverable states that the support should not be carbon. A more stable support is required, but also one which is sufficiently conductive to give acceptable performance. Whilst there has been considerable effort expended looking for such a material, no obvious candidate has emerged. All more stable materials tend to either have insufficient conductivity or surface area or both. However since it is the surface properties of carbon which are responsible for this corrosion, a support with no carbon on the surface would be a possible "non-carbon" support. This raises the possibility of a suitable composite material in which the bulk is highly conductive carbon, but this is protected by a conformal coating of another more stable, but less conductive material. Since the protective material would only be present as a relatively thin layer, this could be significantly less conductive than carbon without impacting the overall conductivity of the composite support adversely. This approach has been exemplified in this project by the atomic layer deposition (ALD) of platinum onto carbon nanofibres which had previously been ALD-coated with a conductive oxide layer.

Another possibility is that the platinum film formed on the support is defect free and sufficiently thick that the support is completely protected by the platinum. This approach therefore allows the use of relatively unstable supports. This has been exemplified by the coating of base metal nanowires by platinum using galvanic displacement.

2 Task 4.1: Preparation of low Pt Loading catalysts

2.1 Johnson Matthey Fuel Cells

The work carried out by JMFC in this task focussed on the development of Pt ALD onto conductive oxide tie layers which had been selected as suitable for use in fuel cell applications.

<u>Wafer Supports</u>

The initial tranche of work focussed on Pt ALD onto an oxide tie layer on silicon wafers. The aim of this work was to derive a process capable of giving a percolating film of contiguous particles at the lowest possible film thickness. In pursuit of this goal a wide range of processes were investigated with the established ALD process of alternating pulses of oxygen and trimethyl(methylcyclopentadienyl) platinum(IV) at 300 °C as a starting point .

Throughout this work the loading of platinum on the surface was determined by XRF and the connectivity of the film inferred from four point probe measurement of the surface conductivity. Subsequently, high resolution SEM images of particularly interesting samples were generated. An SEM image of a typical Pt deposit on an oxide coated silicon wafer is shown in Figure 2.2.1.
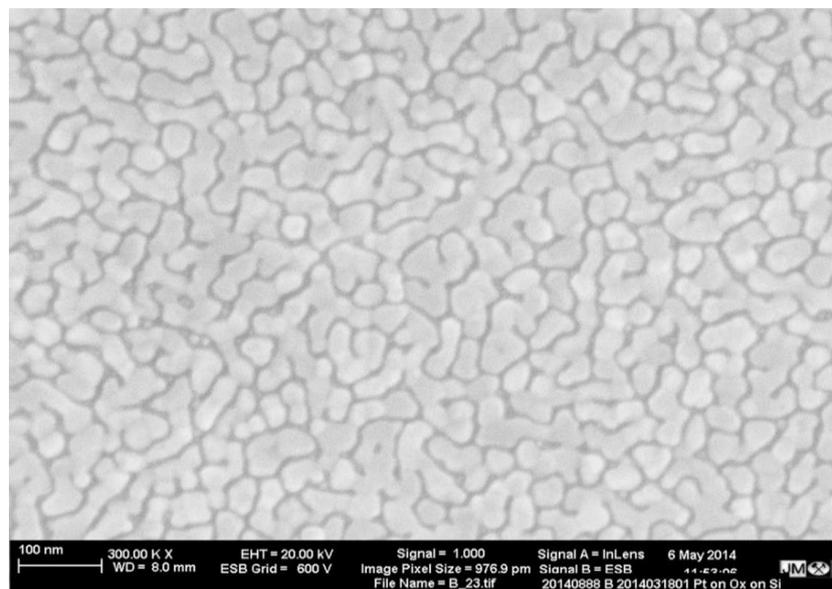

Figure 2.1.1: Electron micrograph at 300k magnification showing the morphology of ALD platinum on oxide coated silicon

In this case the film is not percolating despite the very high coverage of the platinum film. This distinctive morphology is what would be generated if the initial small platinum deposits are mobile on the surface and agglomerate into larger, immobile deposits. This unfortunately means that the surface coverage at which percolation will occur is very much higher than would be expected for random deposition of immobile species onto the surface.

Various changes to the process temperature timings and gases used were investigated. It was found that whilst the process used, and to a lesser extent the substrate used, to receive the Pt caused variations in the platinum loading achieved for a given number of ALD cycles, all the results for conductivity appeared

to fall on a general curve, showing that percolation in the film occurred at 4-5 nm film thickness. This relation is shown in Figure 2.1.2.
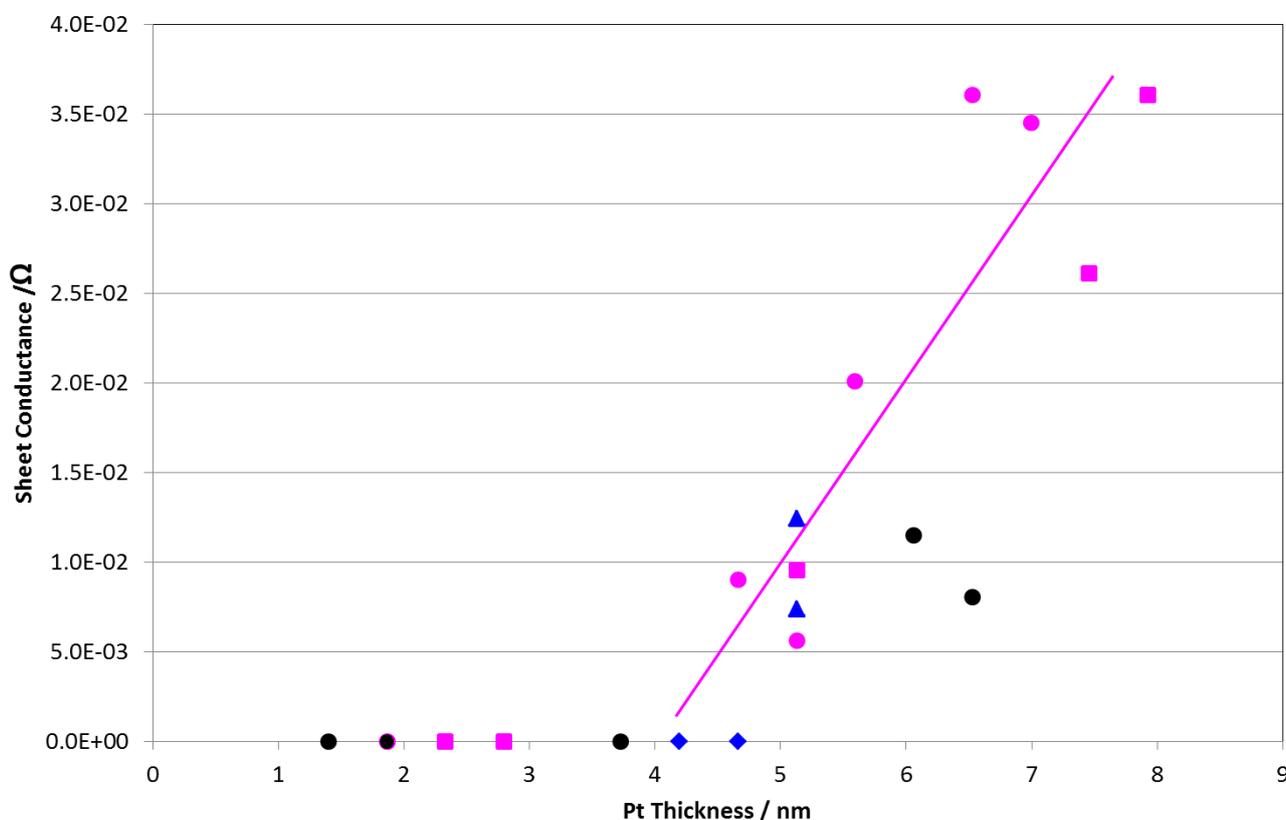

Figure 2.1.2: Dependence on the sheet conductance (as measured by four point probe) on platinum film thickness

The result that percolation can occur at such a low film thickness is an encouraging result. In order to reach the mass activity target of 0.15 A/mg Pt at this film thickness the specific activity of the film would have to be 1400 μA/cm². This is a high value but is the value achieved for polycrystalline platinum and therefore a reasonable expectation for an extensive film.

Another variable which could reasonably be expected to change the nature of the Pt deposit is the Pt precursor used. To this end a known platinum complex was synthesised and assessed for suitability as an ALD precursor. It was found not to be suitable as thermal decomposition occurred prior to sublimation.

Oxide-Coated Carbon Nanofibres

Techniques have been developed to allow the ALD coating of webs of oxide coated carbon nanofibres (supplied by VTT). Due to the fragility of the fibres the gas flows in the ALD tool had to be adjusted greatly, but once this had been done it was found that intact webs of 5cm by 5cm could be coated with reasonable uniformity. Some point to point variation in the platinum loading was found but this was ascribed to variation in the support material rather than a poor ALD process.

Doped Oxide Nanofibres

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UM2 generated a range of doped oxide nanofibres using electrospinning. Whilst these fibres are self-supporting they are extremely fragile. It was therefore impossible to coat them using the ALD in the same way as the oxide coated carbon fibres. A powder coating accessory was therefore used. In this, the sample is held in a pair of glass cups with fritted bottoms through which the process gas flow is directed. Somewhat surprisingly, the oxide nanofibre samples survived coating runs in this accessory intact. They however became completely pulverised by subsequent handling. The webs broke into small flakes of a few millimetres at most, although these flakes still comprised the material in the form of nanofibres.

Due to the pulverisation of the sample prior to XRF measurements an assessment of the uniformity of coating was impossible, but the sample colour is modified by the platinum and this colouration looked uniform suggesting uniformity of the coating.

2.2 Beneq Oy.

Beneq carried out successful ALD coating of both the oxide coated carbon nanofibres and the oxide nanofibres. As was found by JMFC the oxide nanofibres were too fragile for conventional coating techniques. The approach adopted at Beneq was to immobilise the oxide fibres onto adhesive kapton tape. The bulk of the ALD coated samples tested during Task 4.2 were generated by Beneq.

2.3 Université Montpellier 2

Galvanic displacement can be used to exchange peripheral metal ions with ions from another metal with a higher reduction potential. This opens the possibility of forming a thin shell of platinum around nanofibres fabricated using less expensive, more abundant metals than platinum. Base metal nanofibres were used as the substrate for this process. TEM results suggested that the platinum deposited uniformly across the surface of the nanowires but in the form of nanoparticles rather than as a continuous film.

3 Task 4.2: Characterisation and understanding of novel catalysts

3.1 Johnson Matthey Fuel Cells

JMFC has used 2 techniques to determine the mass activity of the novel catalysts in this project, the widely used rotating disc electrode and the more novel floating electrode method. Whilst the rotating disc electrode (RDE) is a widely used technique it is not entirely straightforward and tends to suffer from results varying widely from lab to lab and poor comparability of the results from different supports. Recent RDE results from JMFC have been poor but during the course of the work undertaken in this project the quality of the results has improved to give agreement with previously published work from JMFC for standard JM catalysts (0.21 A/mg Pt @ 0.9 V). The activities are still somewhat lower than have been published by other groups for the same catalysts, however. The recent improvement has been an increased focus on cleanliness of the system and the application of acidified permanganate solution as a cleaning agent.

The floating electrode technique has only very recently been developed (Kucernak *et al.* PCCP <u>15</u> 4329-4340). It offers the promise of mass activity results less dependent on the ability of the experimentalist to form a "good" layer. "Good" in this context means covering the electrode completely and being of a structure which does not generate mass transport losses during the activity test, since oxygen supply to

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the catalyst is in the gas phase rather than the dissolved phase. However, since the same very small quantities of catalyst are used the floating electrode still demands a very high level of cleanliness. JMFC has been developing the floating electrode test during the course of this project and has got to a point where the results are reasonably reproducible. For a standard catalyst, different to the one used in the RDE, a value of 0.61 A/mg Pt @ 0.9V with a standard deviation of 0.1 A/mg Pt could be obtained from a set of 6 repeat measurements. This degree of scatter is acceptable but there does appear to be a significant discrepancy between the values from the floating electrode and those from RDE, which makes direct comparison difficult. This has been observed previously by the original developers of the technique. Another limitation of the technique is that it requires an independent measure of the surface area of the catalyst. This is because the making of the electrode does not use a pre-determined volume of ink, as the RDE preparation method does. Arguably however, the floating electrode gives a more realistic measure of the *possible* mass activity of a catalyst, because of the gas-phase supply of oxygen coupled to a very low loading.

RDE measurements were carried out at 30 °C in 0.1M perchloric acid with a scan rate of 20 mV/s and a rotation rate of 1600 rpm and the results taken from the second anodic scan. The electrochemically accessible metal surface area was measured using cyclic voltammetry using the hydride UPD region.

The first variant of Pt on oxide coated carbon nanofibres gave a mass activity of 0.03 A/mg Pt @ 0.9 V, a specific activity of 45 μA/cm² Pt and a specific area of 67 m²/g Pt. This activity value is low, even if the Pt deposit is not a highly active extensive surface, as desired, a higher specific activity would be expected. The specific area is reasonable for nanoparticulate platinum implying that the loading has not been miscalculated, so the disappointing mass activity is a result of a poorly active surface.

Floating electrode determination of the ORR activity of the Pt on oxide coated carbon nanofibres has been carried out for the same samples as tested by RDE and one with a higher coverage of platinum.
The mass activities are 0.15 A/mg Pt @ 0.9 V for the higher coverage sample and 0.06 A/mg Pt @ 0.9 V for the materials that was also tested by RDE. The first result exceeds the numerical target in Milestone 2, but the milestone also states that the activity should be superior to nano-particulate platinum on carbon. The reason for this conflict is the systematic deviation between floating electrode results and RDE results. In general floating electrode results seem to be about 3 times higher than the same material in an RDE and the comparable activity for Pt/C is 0.66 A/mg Pt @ 0.9 V. Therefore this result exceeds the target numerically, but does not really fulfil the target in the spirit intended.

3.2 Technische Universität München

Both Pt on oxide coated carbon nanofibres and Pt on doped oxide fibres have also been tested for ORR activity using RDE at TUM. Platinum mass content, crucial for determination of mass activity, was determined by external ICP analysis and by XRF measurements at JMFC.

3.2.1   Electrochemical Measurements and acitivity determination

Table 3.2.1: Measurement protocol for catalyst evaluation in 0.1 M $HClO_4$ electrolyte in a three-compartment cell thermostatted at 25°C. In Step 2 and 4, the cathodic vertex potential depends on the catalyst material and can range from 90 to 10 mV (x: 9 − 1), depending on HER onset. Calibration of the reference electrode against the reversible hydrogen electrode and impedance measurement follow step 4.

Step		Sat. gas	Potential window [V] vs. RHE	Start Volt. [V] vs. RHE	Scan rate v [mV/s]	Rotation [rpm]	# of cycles
1.1	CV	Ar	0.05 – 1.1	-	100	200	until stable
1.2	CV	Ar	0.05 – 1.1	-	50	200	5
1.3	CV	Ar	0.05 – 1.1		50	0	3
2	CV	Ar	0.0x – 1.1	0.5	20	0	2 per lower vertex pot.
3.0	CV	O_2 (sat. process)	0.05 – 1.1	0.5	50	1600	until $i_{lim.}$ stable
3.1	LSV	O_2	1.1 – 0.05	1.1	50	1600	3
3.2	LSV	O_2	1.1 – 0.05	1.1	5	1600	3
3.3	LSV	O_2	1.1 – 0.05	1.1	20	1600	3
3.2	LSV	O_2	1.1 – 0.05	1.1	10	1600	3
4	CV	Ar	0.5 – 0.0x	0.5	20	0	2 per lower vertex pot.

Electrochemical measurements were based on procedures described in deliverable D 4.2 and are summarised here as well. All glassware is extensively cleaned before measurements, electrodes are polished and cleaned. The following chemicals were used for the measurements: perchloric acid (70 %, GFS Chemicals, Veritas double distilled), 5 wt% Nafion 110 EW (Sigma Aldrich), potassium hydroxide (Sigma Aldrich, trace metal grade) and propan-2-ol (Sigma Aldrich, HPLC grade). Ultra-pure water (UPW, 18 MΩ·cm, 3 ppb TOC) is made by a Merck Millipore System. Inks were prepared with an Ultrasonic Horn (Branson Digital Sonifier 250, 1/8" tapered microtip).

All inks consisted of pure isopropanol (IPA), with catalyst loadings of 1 − 2 mg/mL, depending on the amount of material available. Higher ink loadings would have been desirable, but the amount of material available from initial ALD depositions at Beneq was too low. Before and during ultrasonic horn treatment (10 min, 25 % amplitude) inks were cooled in an ice bath. To ensure suspension, inks were kept in an ultrasonic bath until the deposition of ink onto a glassy carbon disk had taken place. Catalyst films had to be coated in multiple steps onto the disks to reach the desired loadings and were dried under air. Dilute Nafion solution was added after catalyst films were dried. Electrodes were wetted prior to measurement with water.

Table 3.2.1 gives the measurement details. Electrochemical Surface Area (ECSA) was determined from step 4, where the mean of adsorption and desorption charges was used. For conversion to Pt surface area, the value of 210 µC/cm² Pt was employed. All activities for the oxygen reduction reaction (ORR) are mass transport corrected and reported at 1600 rpm, 0.9 V (iR corrected) vs. RHE.

3.2.2   Pt on oxide coated carbon nanofibres

The results obtained for the Pt on oxide coated carbon nanofibres are shown in Table 3.2.3. By way of comparison a conventional Pt/C catalyst gave a mass activity of 0.27 A/mg Pt @ 0.9V. It is therefore clear that neither sample has reached the target, although the low loaded sample is reasonably close to the required 0.15 A/mg Pt. The specific activities reported are in the normal range for Pt nanoparticles so these results imply the formation of a nanoparticulate Pt deposit. The relative activity of the low and high Pt loadings is the reverse to that seen in the floating electrode at JMFC. The reason for this is unclear.

Table 3.2—2 Activities for Pt on oxide coated carbon nanofibres

Pt loading	v [mV/s]	ECSA [m^2/g_{Pt}]	A_M [A/mg_{Pt}]	A_S [$\mu A/cm^2_{Pt}$]
High	10	30.5±3.1	0.065±0.005	216±32
Low	10	110.8±6.7	0.121±0.02	111±27

3.2.3   ALD Pt on oxide nanofibres

Two platinum loadings were studied on doped oxide nanofibres. On the lower loaded sample no ORR activity could be measured at all. On the higher loaded sample the activity was measureable but it was very low given the high level of platinum on the sample. The cyclic voltammograms obtained for this sample were anomalous with a strong shift in the position of the peaks associated with platinum oxide formation and reduction. This suggests that the platinum is forming an alloy with the metal of the oxide.

3.3   Université Montpellier 2

UM2 activity tested the Pt coated metal nanowires that they generated using galvanic displacement. Two variants were tested. The first was prepared by a standard galvanic displacement process, whereas the second was made using a novel improved process. This was found to result in a more rapid deposition of platinum.

The standard process lead to a calculated activity of 0.012 A/mg Pt @0.9V, but during the course of the experiment it could be seen that the samples was degrading and not really giving any stable performance, so even this low value should be treated with caution. For the sample generated using the improved process a stable and much higher activity of 0.042 A/mg Pt @ 0.9V was found. This value does not seem that impressive, but a commercial Pt/C tested by UM2 at the same time gave activities in the range of 0.040-0.045 A/mg Pt @0.9V and thus the coated nanowires are at least as good as the conventional catalyst.

To assess the stability of the more active sample it was cycled between 0.6V and 1.0V in the presence of oxygen and the change in the platinum surface area monitored by cyclic voltammetry. The platinum surface area decreased by 48% which is an encouragingly low amount. Since the support material for this sample is a highly corrodible base metal this must mean that it is substantially, or possibly completely, covered by the platinum.

The stability and mass activity comparable with commercial Pt/C catalysts together with the high speed of the improved galvanic displacement process suggest that this may be a first step towards a scalable process capable of producing stable catalysts with low Pt loading, which could reach the mass activity target. Process optimisation will be performed to increase the mass activity and stability, and tune the Pt loading, as well as HR-TEM evaluation of the Pt morphology.

4 Task 4.3: Catalyst layer and MEA development

4.1 Johnson Matthey Fuel Cells

Due to the very limited quantities of catalyst available so far in CATAPULT novel MEA preparation techniques needed to be developed, even though novel materials will be cell tested as small 6 cm² MEAs. Conventional ink-based techniques require much more catalyst, very little of which actually ends up on the active area of the MEA. What is required here is a technique which utilises almost all of the catalyst. If this is achieved the current rate of production of the novel catalysts can produce enough to produce sufficient MEAs to allow systematic development and optimisation of the cathode catalyst layer. A single ALD run could produce enough catalyst for a few 6 cm² MEAs or one 50cm² MEA. With the catalyst utilisation of conventional techniques huge amounts of preparative effort would have to go towards creating a single small area MEA.

In order to create a good catalyst layer the catalyst must be effectively broken up and dispersed in a liquid medium and a suitable amount of ionomer added, which will then adsorb onto the surface of the dispersed catalyst. The dispersion method which requires the smallest volume of liquid is an ultrasonic horn. This can be used on volumes as small as 2 ml. Even at this volume this will produce an ink that is much more dilute than a standard ink for printing or coating, it will be completely inviscid (viscosity = zero) and thus will have to be spray coated. It is known that if a coating of an inviscid ink ever accumulates a significant wet film thickness during deposition then on drying an inhomogeneous layer will be formed with catalyst only in the areas which were the last to dry, the so-called "coffee ring effect". To avoid this, spray coating should be carried out onto a heated substrate at a rate such that a significant wet film is never formed.

As a result of the considerations outlined above the following procedure was adopted. The required amount of catalyst, usually a few square centimetres of web, was placed into 2-3 ml of propan-1-ol. This was then sonicated with the ultrasonic horn for a total of 10 minutes. Sonication was applied in 10 second pulses with 20 seconds rest in between to avoid overheating. During this the web was completely disintegrated and formed a stable suspension in the solvent. Nafion 1100 EW ionomer dissolved in a mixture of alcohols was then added. The amount of ionomer was calculated to give a 6 nm film on the entire surface of the catalysed support. This calculation requires the weight of the catalyst, a density value determined from the known composition of the catalyst and a fibre diameter. The density and fibre diameters were approximate values so there is a certain amount of error in this calculation. The dispersion containing the catalyst and ionomer was then sonicated again using the same conditions. This produced the final ink.
A 50 cm² standard Pt/C anode was decal transferred from PTFE onto a 10 cm x 10 cm piece of reinforced PFSA membrane using hot pressing. This "half-CCM" was then placed on a PTFE sheet on a hotplate at

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90 °C, a PTFE mask with a 3 cm x 2 cm hole in it was then placed over the top of this. The ink was then sprayed onto the membrane area exposed through the hole in the mask using an air brush. In this preparation method the only way that catalyst in the ink does not get onto the active area is through overspray. It was therefore thought that catalyst utilisation would be very high. This was however not found to be true. Initial attempts produced a yield of 2% resulting in very low loaded MEAs which could not be cell tested. A smaller more accurate gravity fed airbrush was then used and this yield could be increased to 20% still well below expectations. This still resulted in MEAs with loadings so low that testing was possible, but was still compromised.

As a result of the problems observed with the ink-based routes, direct lamination of the catalysed web onto the membrane was used. This approach has previously been used with reasonable success at JMFC but means that the form of the web has to be controlled to optimise catalyst layer structure, which is not always that easy to do. This approach is not suitable for the oxide nanofibres from UM2 as they are simply too fragile to be assembled reliably. After direct lamination of the web onto the MEA the ionomer was added to the catalyst layer by pipetting on the required amount of ionomer in 1-2 ml of propan-2-ol on the catalyst layer and leaving it to dry.

The mass activity of the MEA is determined using SSK2 as defined in the CATAPULT deliverable 2.1. This is at 170 kPag pressure running the cell on H_2/O_2 at 80°C and 100% relative humidity. Figure 4.1.1 shows the results from an MEA made *via* the ink-based route from the oxide coated carbon nanofibre web coated with 25 ALD cycles of platinum at Beneq. The platinum loading was 32 µg Pt/cm^2 MEA, well below the target of 100 µg Pt/cm^2. The data is plotted as a log-linear "Tafel" plot of iR-corrected voltage *vs.* crossover-corrected current. The voltage has been corrected for the iR ohmic losses in the membrane using a current interrupt resistance measurement measured automatically during the experiment. The crossover correction is required to correct for the contribution of the current from hydrogen crossover. This is determined by measuring the current generated in the MEA at voltages from 0.2 V to 0.4 V whilst hydrogen is flowing on the anode of the cell and oxygen on the cathode. These currents are then plotted and extrapolated back to zero current. This gives the current arising from hydrogen crossover, which is added to the measured current to give the current being generated by the ORR reaction.
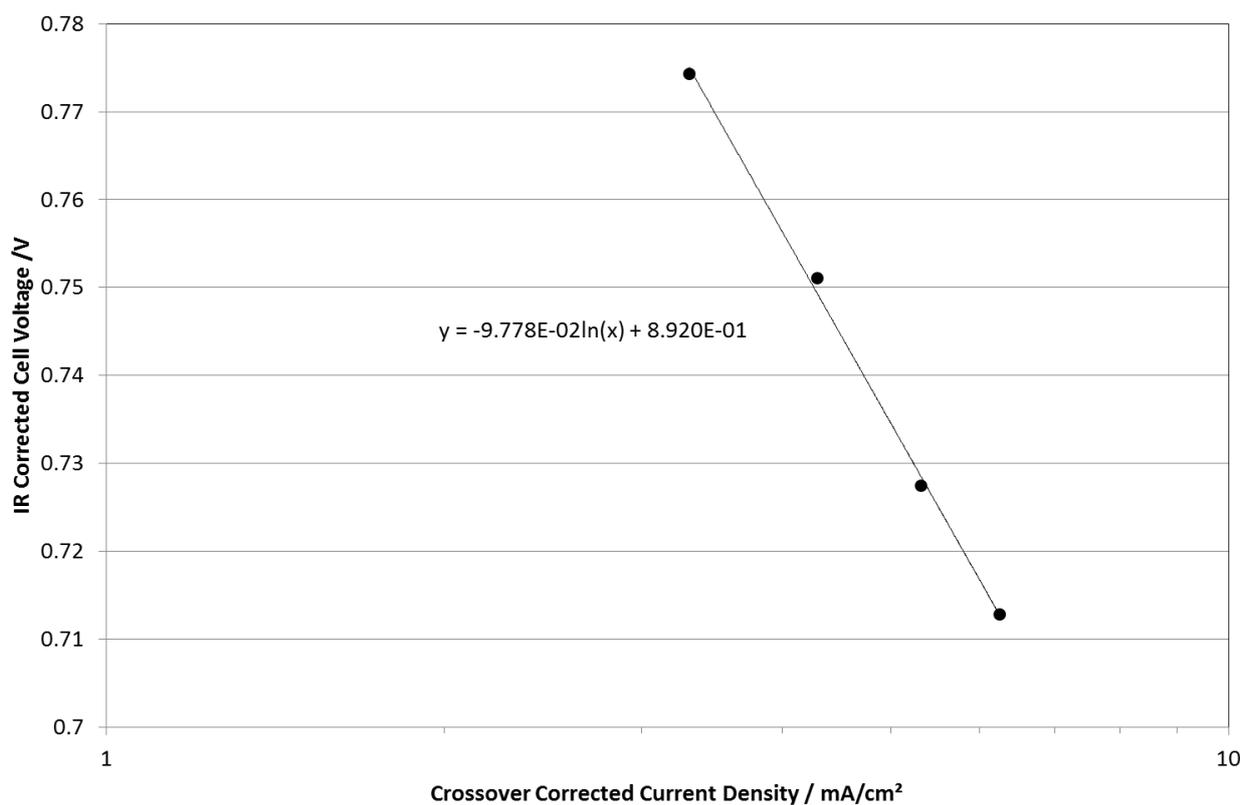
$$y = -9.778E\text{-}02\ln(x) + 8.920E\text{-}01$$

Figure 4.1.1: MEA performance of Pt on oxide coated carbon nanofibres spray coated to give a platinum loading of 32 µg Pt/ cm² tested under conditions of SSK2

The fit line to the data shown in Figure 4.1.1 was used to extrapolate to the expected performance at 0.9 V. The good quality of the fit is in agreement with the assumption that the performance of the MEA in this current range is purely controlled by the reaction kinetics and that these are following the expected Butler-Volmer equation. As can be seen the low loading of the sample resulted in the extrapolation being much bigger than would be normally expected. Ideally, data would be collected actually spanning 0.9 V to allow more reliable determination of the activity, however this was not possible in this case. The current densities used to collect this data were very low and reducing them further would degrade the quality of the data unacceptably. The mass activity determined from this data was 0.03 A/mg Pt @ 0.9 V.

Whilst the MEA was in the cell the electrochemically active Pt area was determined by cyclic voltammetry after CO poisoning. The area of the distinctive CO oxidation peak can be used to derive the metal area. This produced a calculated specific activity of 190 µA/cm² Pt. This is a reasonable value for nanoparticulate platinum. The specific surface area of this sample derived from the same metal area is 15 m²/g Pt. This is a very low value for nanoparticulate platinum suggesting that not all of the platinum in the sample is electrochemically active. This means it is electrically isolated due to it not being connected by the ionomer to a proton conducting path or due to the support not being sufficiently conducting to connect it to an electronically conducting path.

Figure 4.1.2 shows the plot of iR corrected voltage against crossover-corrected current for a sample made by direct lamination of the oxide coated carbon nanofibre web coated with 10 ALD cycles of platinum at Beneq.
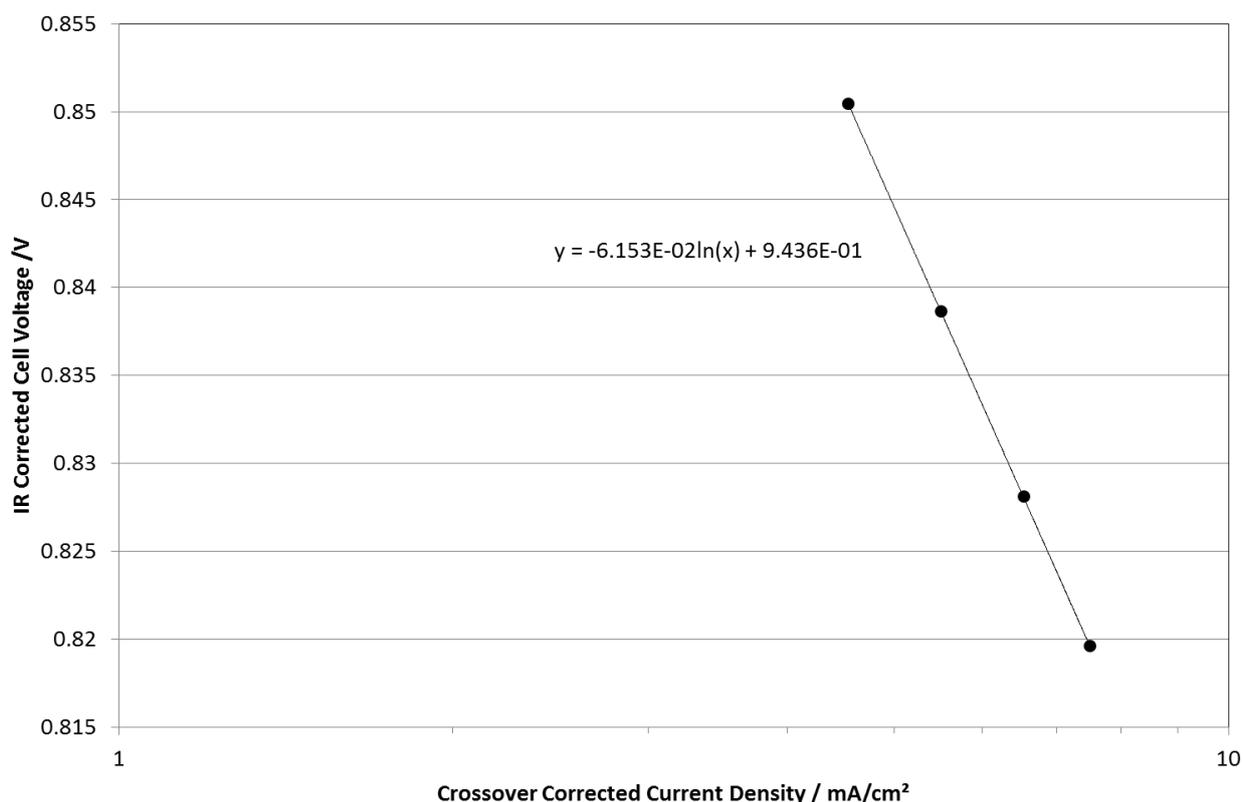
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Figure 4.1.2: MEA performance of Pt on oxide coated carbon nanofibres directly laminated onto a membrane to give a loading of 100 µg Pt/cm² tested under conditions of SSK2

The mass activity determined from the data in Figure 4.1.2 is 0.02 A/mg Pt @ 0.9 V, the specific activity 90 µA/cm² and the specific area 23 m²/g. Again this surface area seems low and RDE measurements on the same material presented above in Section 3.1.1 give a more reasonable area of 67 m²/g. This again suggests some of the platinum is not being accessed; even allowing for this the specific activity is a low value meaning that even the platinum that is electrochemically active is not functioning as well as one might expect. The same sample was tested at higher current density than those shown in Figure 4.1.2 to see if using more usual current densities produced better results. These results are shown in Figure 4.1.3. The activities generated from these results are 0.04 A/mg Pt @ 0.9V and 170 µA/cm². These are slightly more encouraging; the specific activity being in the range expected from nanoparticulate platinum. If, as suggested by the low specific area, some of the platinum is not electrochemically active in this test it could be argued that the mass activity should be scaled upwards by the ratio of the measured area to the more reasonable area. This would give a value of 0.12 A/mg Pt, approaching the target of 0.15 A/mg Pt. It should however be noted that the log-linear fit in Figure 4.1.3 is of poorer quality than those in Figures 4.1.1 and 4.1.2 suggesting that the assumption of pure kinetic control is breaking down and therefore that the determination of activity from this data is suspect. If the better looking data in Figure 4.1.2 is used, even with the scaling to account for inactive platinum the mass activity is only 0.06 A/mg Pt. The RDE measurements above give a mass activity of 0.03 A/mg Pt, which agrees reasonably with the MEA result of 0.02-0.04 A/mg Pt, but the RDE specific activity of 45 µA/cm² Pt does not agree as well.

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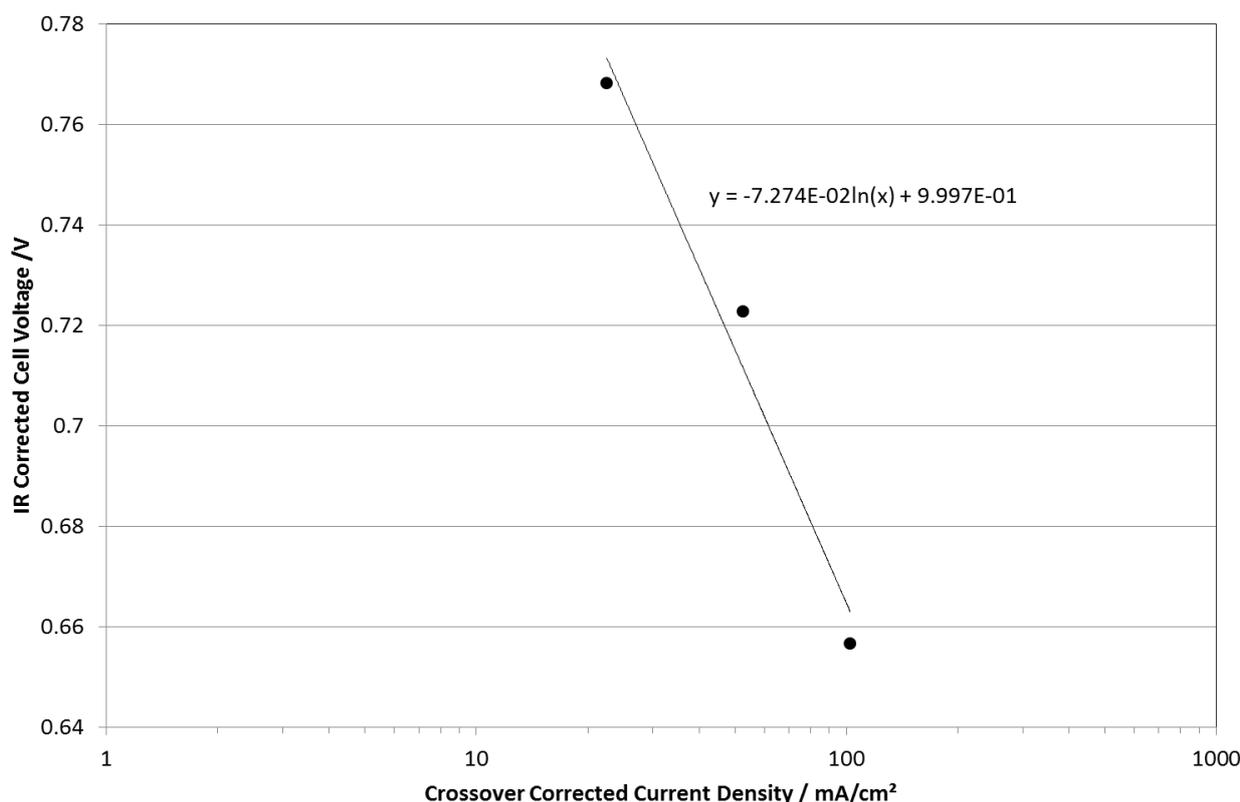$$y = -7.274E\text{-}02\ln(x) + 9.997E\text{-}01$$

Figure 4.1.3: MEA performance of Pt on oxide coated carbon nanofibres directly laminated onto a membrane to give a loading of 100 µg Pt/cm² tested under conditions of SSK2 at higher currents than Figure 4.1.2

Figure 4.1.4 shows a comparison of the performance of the MEA formed by direct lamination of the Pt on oxide coated carbon sample to the standard CATAPULT MEA on the SAE standard air polarisation test, which is the CATAPULT SSK3 protocol. It can be seen that the conventional MEA has a significantly higher performance. Some of this difference can be attributed to the higher platinum loading (400 µg/cm² *vs.* 100 µg/cm²), some to the higher mass activity of the platinum in the standard MEA, but it can be seen the most of the performance difference is due to the very different gradients of the 2 polarisation curves. Whilst it is not trivial to assign losses when comparing polarisation curves, a difference in gradient at higher current densities is not primarily a kinetic activity problem. Mass transport or ohmic losses are much more likely to be responsible.
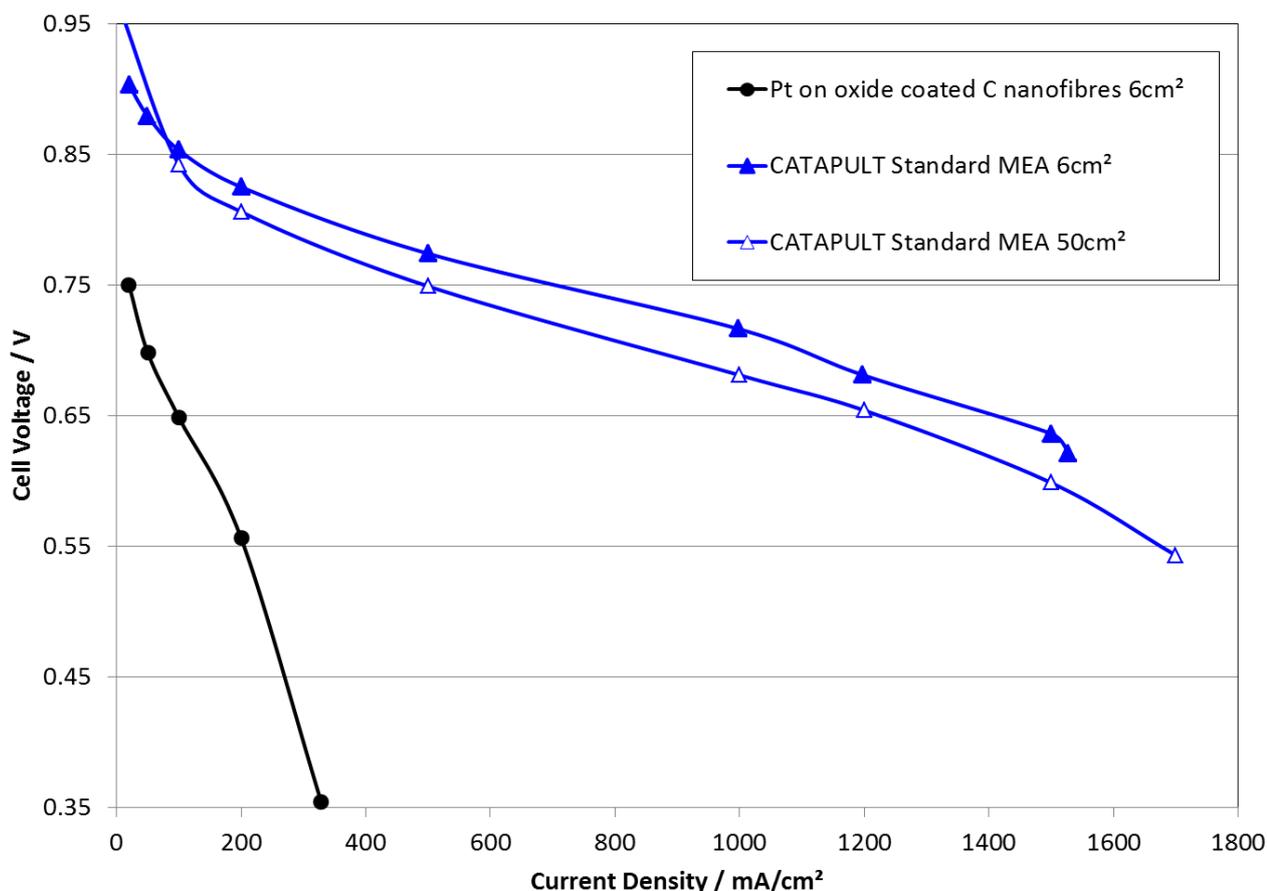
CATAPULT Deliverable Report D.4.4 –DEMONSTRATION OF PT-CATALYSED NON-CARBON SUPPORT WITH HIGHER MASS ACTIVITY THAN CONVENTIONAL PT/C NANOPARTICLES AND IN EXCESS OF 0.15 A/MG PT

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Figure 4.1.4: Comparison of the SSK3 air polarisation test performance of CATAPULT standard MEA and Pt on oxide–coated carbon nanofibres directly laminated onto a membrane to give a loading of 100 μg Pt/cm²

5   Summary and Conclusions

The milestone associated with this deliverable (MS2) is intended as a target to assess the catalytic activity of the novel catalysts produced in this project. The key objective is to determine that the activity is sufficient to make the real goal of the project, a reduction in the mass of platinum per Watt of useful power at the end of life of an MEA, realisable through optimisation of the catalyst layer structure. As can be seen from the data presented above, the precise determination of fuel cell relevant oxygen reduction activity is not straightforward because of variability of results within a particular technique and because of discrepancies between the different techniques. The objective of the work reported in this deliverable was that the mass activity should be both higher than 0.15 A/mg Pt and also higher than conventional Pt/C nanoparticles. One of the materials above achieved 0.15 A/mg Pt, whilst a completely different one showed activity higher than Pt/C nanoparticles.

The most promising mass activity data is clearly that of the Pt-coated metal nanowires produced by the improved galvanic displacement method at UM2. This material provided similar mass activity to Pt/C in a comparable RDE test, although this result requires further verification since the comparative Pt/C activity is very low.

The original aim of the project is also to realise this thin film on a non-carbon support. The base metal of the nanowires conforms to the milestone MS2, however some thought must be given as to whether a

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corrodible metal is a suitable non-carbon support when the overall aim of the project is considered. The reason for avoiding carbon is that it is deemed to be too unstable under true operating conditions therefore the adoption of something as corrodible as a base metal seems a retrograde step. This is not however necessarily true. If the metal support allows a suitably continuous platinum film to form, such that no base metal is electrochemically accessible to the electrolyte, then a stable platinum on base metal catalyst is feasible. The stability data for the Pt coated nanowires is reasonable, but it does not prove that no base metal is removed from catalyst. It is quite possible that base metal is removed from the support during the cycling and the apparent stability is merely a result of the platinum overlayer being relatively undisturbed as the base metal is etched away around it. Base metal being leached into the electrolyte would be much less of an issue in an RDE test, with its massive excess of liquid acid, than it would be in an MEA where it would be reasonable to expect base metal ions in the ionomer either in the catalyst layer or in the membrane would have a detrimental effect. However it must be said that the extent to which base metal impurities can reduce MEA performance is an active and controversial area of study and certainly good performance can sometimes be obtained in the presence of base metal.

It is therefore clear that Pt coating *via* galvanic displacement onto base metal nanowires certainly merits further work, firstly to confirm the activity and stability, preferably in an MEA.

The material which achieved the numerical target of 0.15 A/mg/Pt is the Pt on oxide coated carbon nanofibres from VTT. This result was however obtained in the floating electrode test where a conventional Pt/C would have a much higher activity (0.66 A/mg Pt). Therefore it must be admitted that whilst this result hits the numerical target it cannot be considered to have achieved the more important target of outperforming Pt/C in a comparable test. This assertion is confirmed by the RDE tests on the same material carried out by both JMFC and TUM. There is not particularly good agreement between all the measurements on the Pt on oxide coated carbon nanofibres, but taken as the whole the body of results presented above suggest that the activity is below a conventional Pt/C, although TUM RDE measurements on the material with the lower platinum loading suggest that it may be only slightly less active. This result does require ICP confirmation of the Pt loading, data which was not yet available at the time of writing this report.

The reason why these materials have not achieved the expected mass activity is that in these samples the original concept of this project has not been achieved. Figure 5.1 (provided by VTT) shows a high resolution image of the surface of a Pt on oxide coated carbon nanofibre sample. It is clear that instead of the extensive connected platinum deposits envisaged isolated platinum nanoparticles of 2-5 nm have been formed. In order to maximise the mass activity of a structure of the type shown in Figure 5.1 the temptation would be to reduce the particle size of the platinum to increase the specific area of the metal. This was attempted in later ALD trials at Beneq and the TUM RDE results suggest it was successful. However this approach would result in optimising this structure to the same local maximum of activity as existing technology, whereas the aim of this work was to investigate the possibility of another maximum where bigger but more extensive Pt deposits have a better specific activity which can compensate for a lower specific metal area. The poor results from the VTT materials do therefore not invalidate the underlying thesis of this portion of the project. The issue is that the materials created to date have not embodied the concept. It has not been shown that extensive Pt deposits cannot give a high mass activity. Indeed the results from UM2 presented above suggest that this is possible, as does work by General Motors where Pt films are formed on a tungsten underlayer (Patent US 8,647,723).
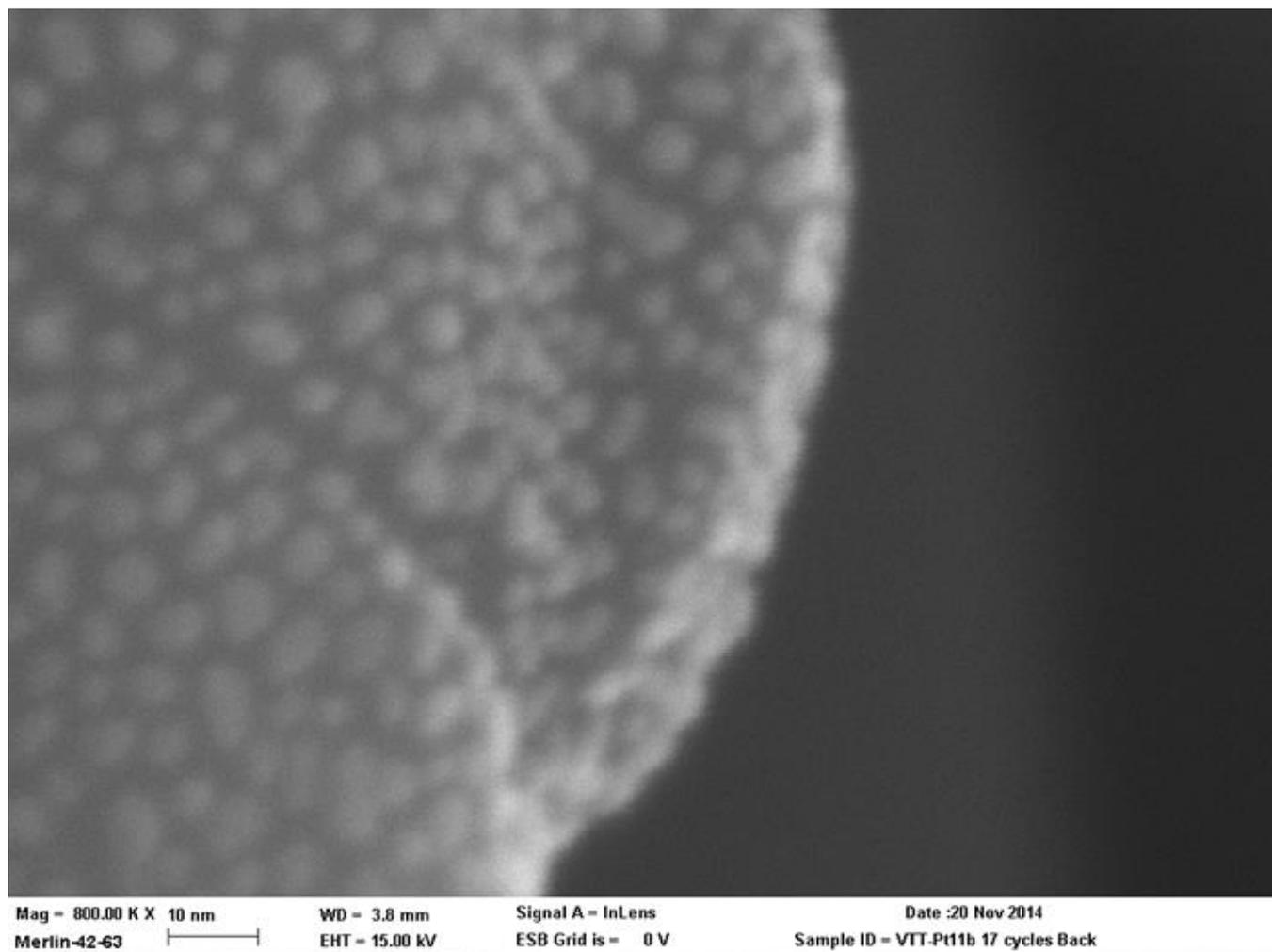
| Mag = 800.00 K X 10 nm | WD = 3.8 mm | Signal A = InLens | Date :20 Nov 2014 |
| Merlin-42-63 | EHT = 15.00 kV | ESB Grid is = 0 V | Sample ID = VTT-Pt11b 17 cycles Back |

Figure 5.1: Electron micrograph of ALD Pt on oxide coated carbon nanofibres

Clearly then the aim of the future work in this area should be to create larger platinum deposits which are contiguous on the support surface and ideally form a complete film. There are two ways to approach this; changes to the ALD process and changes to the support surface. The most straightforward change to the ALD process would be to investigate the effect of more cycles of platinum. To this end samples with more cycles of platinum on the oxide coated carbon nanofibres have been prepared and will be tested. It may seem counter-intuitive to expect that these materials will be more active but it is not impossible that the gains in specific activity to be had from bigger platinum particles can outweigh the loss in specific area as the particles grow. This will be especially true if the particles coalesce. Conductivity measurements on flat substrates show that film percolation causes a massive rise in surface conductivity for these materials. This would be expected to be beneficial to activity and would also address one of the possible causes of the unacceptably high layer losses seen in Figure 4.1.3.

It was originally envisaged that a number of different support surfaces would be assessed to select one on which platinum nucleates and spreads the best. To date the only one has been investigated electrochemically and whilst it has been proved to be reasonable, more candidate materials should be investigated, ideally based on the results of the simulations in deliverables 6.4 and 6.5.

The oxide nanofibres appear to show low or no activity due to alloy formation at the high temperature used for Pt ALD so, despite their high conductivity and their featuring in the simulations of deliverables 6.4 and 6.5, must be considered to be the least interesting of the current approaches. It should be noted that platinum deposition on similar oxide materials *via* chemical methods has been shown to not generate inactive alloys.

The mass activities of the more promising materials tested along with comparative results for conventional Pt/C catalysts are summarised in Table 5.1

Table 5.1: Mass activities reported in this deliverable and comparative data from Pt/C

Pt Deposition Method	Support	Mass Activity A/ mg Pt	Measurement Technique	Pt/C Mass Activity A/ mg Pt
Improved galvanic displacement	Metal nanowire	**0.042**	RDE (UM2)	0.043
ALD Low loading	Oxide on carbon	**0.14**	RDE (TUM)	0.27
ALD Low loading	Oxide on carbon	**0.03**	RDE (JMFC)	0.21
ALD Low loading	Oxide on carbon	**0.06**	Floating Electrode (JMFC)	0.66
ALD High loading	Oxide on carbon	**0.07**	RDE (TUM)	0.27
ALD High loading	Oxide on carbon	**0.15**	Floating Electrode (JMFC)	0.66

Due to the complex nature of the target associated with this report and the complexity of the measurements involved it cannot be said that the target has been unambiguously achieved. What is however clear is that materials of sufficient promise have already been created and that these merit further study in MEAs as part of Task 4.3. It is also clear that the techniques for characterisation have been established and although results can be difficult to compare the accuracy is sufficient to compare new materials generated by the ongoing activities on Task 4.1 well enough to decide which ones to progress to MEA testing.