



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

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DELIVERABLE REPORT

D3.1 – REPORT ON ACTIVITY AND STABILITY OF REFERENCE CATALYST

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Author(s)	Ludwig Asen, Sladjana Martens, Oliver Schneider, Giorgio Ercolano, Deborah Jones, Chris Zalitis, Alex Martinez Bonastre, Jonathan Sharman, Fabio Dionigi, Peter Strasser
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NATURE OF THE DELIVERABLE

R	<i>Report</i>	X
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O	<i>Other</i>	

SUMMARY	
Keywords	Benchmark catalyst, rotating disc electrode, floating electrode technique, testing protocols, stability
Full Abstract (Confidential)	<p>Both a state-of-the-art Pt/C benchmark catalyst and a de-alloyed PtNi/C catalyst were studied for the oxygen reduction reaction at the cathode of the fuel cell, with the rotating disc electrode (RDE) technique, the floating electrode (FE) technique and as complete membrane electrode assembly (MEA) measurements in single cells, in order to define a baseline for catalyst characterisation within the project. For RDE measurements, a detailed testing protocol was developed to enhance the accuracy and comparability of the method, and was validated by experimental investigations. Comparable results for the activities of the Pt/C catalysts between the different laboratories were achieved in the RDE measurements. The kinetic activity of PtNi/C catalyst outperformed the Pt/C catalyst, but the scatter of the data was larger in RDE measurements. Based on the results of MEA degradation studies, a modified procedure for accelerated aging in RDE measurements was developed, that was able to induce activity losses in the supported Pt catalyst without being too harsh for the Pt alloy catalysts. The floating electrode technique delivered similar kinetic current densities at 0.9 V as measured in the RDE, but did not require a mass transport correction, as the limiting currents were several orders of magnitude larger. In this case also mass activities at much lower potentials more representative of actual fuel cell applications were determined, namely at 0.65 V vs. RHE. Measurements of the same benchmark catalysts in small and large size MEAs provided solid data to compare the RDE results to. Good agreement, especially for the Pt/C catalyst was found. Several degradation protocols were tested with small-area MEAs, and the best protocol then validated in large-area MEAs. The PtNi catalyst showed the higher mass activity both at beginning and at end of life. Design criteria that permit down-selecting new catalysts on the basis of their kinetic activity improvements in the RDE and later in MEA measurements were determined.</p>
Publishable Abstract (If different from above)	

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REPORT ON ACTIVITY AND STABILITY OF REFERENCE CATALYST

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1. INTRODUCTION

In order to provide initial validation of newly developed PEM fuel cell cathode catalysts, they need to be tested in a reliable and meaningful way for activity and stability. Ideally, such tests would need to be carried out in a large active area membrane electrode assembly (MEA) in a single cell test configuration. However, for newly developed or modified catalyst materials, preparation of the large quantities needed for MEA fabrication is often not justifiable at this early development stage. In addition, MEA testing is time-consuming, requires adequate instrumentation and accurate control of gas pressures, temperatures and relative humidities. For these reasons, a characterisation method based on the rotating disc electrode (RDE) is normally used instead¹⁻³. A thin catalyst layer is coated onto the polished glassy carbon electrode insert of an RDE, and then the oxygen reduction reaction (ORR) activity is determined from a polarisation curve under rotation at 0.9 V vs. RHE in an oxygenated, aqueous perchloric acid solution.

However, the application of the technique is by no means simple. In the entire experimental chain, from catalyst ink preparation to data analysis, there are many steps that can affect the results obtained. Thus, the method has been discussed intensively in recent literature⁴⁻⁹, with the intention of identifying the pitfalls of the method and to obtain more reliable data. In the past, different laboratories testing the same catalyst have often obtained widely different results.

Therefore, the INSPIRE consortium decided to use data from two benchmark catalysts to act as the basis for comparison with the RDE data obtained from the newly developed catalysts, which are candidates for subsequent stack application. Selection criteria based on activity enhancement, compared to the benchmark catalyst have been formulated for down-selecting a catalyst for single cell MEA testing. A commercial 50 wt% Pt/C catalyst from JM was selected as the benchmark catalyst. In addition, a developmental JM PtNi alloy catalyst, prepared by the “de-alloying” approach with 28.6% Pt was also tested. In order to obtain reproducible and comparable results between the different laboratories, a detailed measurement protocol was established and adjusted based on testing in the laboratories of CNRS, TUB and TUM, the latter also being in charge of drafting the protocol, and input by JM based on their experience from MEA testing. In addition, an accelerated stress test for stability testing was selected, based on data generated at the partners. One of the drawbacks of the RDE method is the low solubility of oxygen in the electrolyte, resulting in diffusion limited current densities of $\sim 6 \text{ mAcm}^{-2}$ at a rotation rate of 1600 rpm. Thus, a correction for mass transport needs to be undertaken to obtain the kinetic current at 0.9 V, and no performance data can be obtained under realistic over-potentials and (mass specific) currents of an MEA. A testing method not having these drawbacks was recently developed by Zalitis et al.¹⁰: Their floating electrode technique results in mass transport improvement by three orders of magnitude. This method was also applied to the benchmark catalysts, in the laboratories of JM, as a collaboration between JM, TUM and TUB.

At JM, benchmark studies were also performed in MEAs, using the same benchmark catalysts, to give a basis of comparison for the MEA testing of down-selected INSPIRE catalysts.

2. EXPERIMENTAL

RDE measurements

The RDE testing protocol that was explored and adjusted in the course of the experimental work contains detailed procedures for all the relevant experimental steps in the testing procedure, including cleaning procedures, reference electrode preparation/calibration, choice of counter electrode, glassy carbon disk polishing, the preparation of the catalyst ink, the application methods for the ink, the loading, the choice of perchloric acid and the electrochemical protocols. Importantly, immersion of the electrode into the electrolyte was always done under potential control, to avoid undefined open circuit exposure. Electrochemical protocols are available for conditioning of pure Pt catalysts, pre-treatment and conditioning of pre-leached Pt alloy catalysts, de-alloying and conditioning of newly developed Pt alloy catalysts, ECSA determination with the H_{UPD} method, impedance spectroscopy, ORR testing and data analysis, and stability testing. The latter comprises a catalyst stability testing protocol, and the investigation of support corrosion.

The experimental setup, the chemicals used and some operating conditions at TUM, CNRS and TUB are given in Table 1 -

Table 3. Further details about the actual measurements are given in the Results section.

Table 1. Chemicals and experimental setups used at TUM for RDE measurements.

Ink Composition 4 mg 50wt% Pt Catalyst (7 mg PtNi catalyst) 7.96 ml H ₂ O 2 ml IPA 40 μ l Nafion (5 wt%) 0.2 mg _{Pt} /ml	Ultrasound equipment Bandelin Sonopulse HD 3200, microtip MS73, outer diameter of horn tip 3mm, 10% amplitude.
Ink Application 10-20 μ l – 10.1-20.2 μ g _{Pt} cm ⁻² 0 or 700 RPM	Ultrasound Treatment 15 min @ 10 % Amplitude in ice bath Additional 40 s prior pipetting
Reference Electrode Reversible hydrogen electrode (RHE)	Calibrated on N.A.
Counter Electrode Pt wire or Graphite Rod	Temperature / °C 25 °C
HClO₄ specification Acros Organics, p.A.	Inert Gas Type and Purity Ar 5.0, Westfalengas
Oxygen gas purity O ₂ 5.0, Westfalengas	Potentiostat Ivium Compactstat Plus
Impedance Spectrometer Ivium Compactstat Plus	RDE Setup Gamry (Pine Instruments) RDE 710, 5 mm ϕ glassy carbon (GC) electrode

Table 2. Chemicals and experimental setups used at CNRS for RDE measurements.

Ink Composition 3.6 mg Catalyst 7.26 ml H ₂ O 1.83 ml IPA 36 µl Nafion 0.197 mg _{Pt} /ml	Ultrasound equipment Branson Digital Sonifier 450 (400W) Tip: Branson Model 102 C (3 mm)
Ink Application 10-20 µl -- 10-20 µg _{Pt} cm ⁻² (2-4 µg _{Pt} electrode) 0 or 700 RPM (60 W Lamp/Heater)	Ultrasound Treatment 15 min @ 10 % Amplitude in ice bath Additional 40 s prior pipetting
Reference Electrode Reversible hydrogen electrode (RHE)	Calibrated on N.A.
Counter Electrode Pt wire or Graphite Rod	Temperature / °C 20 °C
HClO₄ specification Fluka TRACEselect Ultrex II Ultrapure Reagent (JT Baker)	Inert Gas Type and Purity N ₂ Air Liquide Ultrapure 99,999 %
Oxygen gas purity Air Liquide Ultrapure 99,999 %	Potentiostat Biologic SP-300
Impedance Spectrometer Biologic SP-300	RDE Setup PINE RDE ~0.2 cm ² GC Electrode

Table 3. Chemicals and experimental setups used at TUB for RDE measurements.

Ink Composition 2 mg catalyst for Pt/C (3.3 mg for PtNi/C) 3.98 ml ultrapure water 1 ml isopropanol 20 µl of a 5wt% Nafion ionomer solution	Ultrasound equipment Branson Sonifier 150, outer diameter of horn tip 3mm
Ink Application 2 times 10 µl, After each step the ink was dried in an oven at 60°C for ~7 min	Ultrasound Treatment Horn sonifier with a water bath at room temperature
Reference Electrode Mercury/Mercurous Sulfate (MMS)	Calibrated on Every second week vs reversible hydrogen electrode(RHE)
Counter Electrode Pt mesh wrapped on Pt wire	Temperature / °C Room temperature, measured range 22-25°C.
HClO₄ specification 70% conc. HClO ₄ , 99.999% trace metal bases, Sigma Aldrich	Inert Gas Type and Purity N ₂ , 99.999%
Oxygen gas purity 99.999 % (5.0)	Potentiostat Biologic
Impedance Spectrometer Biologic	RDE Setup Pine

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 1100EW (equivalent weight in g polymer/mol H⁺) aqueous ionomer perfluorosulfonic 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 mgPtcm⁻², unless specified otherwise. The anode catalyst layer was kept constant at ionomer/carbon weight ratios ca. 1.5/1 and metal loading of 0.1 mgPtcm⁻². 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 were 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 pressure relief films. After fabrication the active area on each electrode was reduced to 6 cm², (3x2) cm, with the lamination of a seal over the electrode area. Commercially available gas-diffusion layers (GDLs), based on Teflonated 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 an average 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. The specific details for this protocol are shown in Table 4. 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 inlet 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 1kHz at three different current densities of 25, 50 and 100 mA/cm² and also using a current interrupt method. For each data point, the cell voltage was stabilized over 10 min 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 50kPa_{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. Afterwards the cathode catalyst layer was exposed to a series of cathode starvation steps under H₂/air as specified in Table 4 and following the US Department of Energy (DOE) Tech Team fuel cell polarisation protocol but under the pressure and humidity conditions specified in the conditioning step. After the starvation steps the MEA was ready for testing and a series of measurements were performed for each sample. These consisted of a series of H₂/O₂ polarisation curves for mass activity quantification at different stages of the protocol. The polarisation curves were recorded in the descending direction, from high current density (i.e. 2 Acm⁻²) to low current density (i.e. 0.05 Acm⁻²), and the ascending direction, low current density to high current density. The mass activity value was obtained from the ascending polarisation curve and the current density maintained for 3 minutes at each step. Details of such conditions are shown in Table 4.

The measured mass activity was corrected for the measured H₂ crossover. For this study, H₂-crossover current densities were measured under the operating conditions (i.e. temperature and H₂-partial pressure) and catalyst activities were evaluated on the basis of H₂-crossover corrected current densities, i_{eff} (i.e. $i_{\text{eff}} = i + i_x$, with i_x being on the order of 2–5 mAcm⁻²).

Table 4. Test protocol conditions for 6 cm² cell.

	Anode Gas Composition	Anode Stoich.	Cathode Gas Composition	Cathode Stoich.	% RHA	% RHC	Anode Inlet P (kPa _g)	Cathode Inlet P (kPa _g)	Cell Temperature / °C	Current Density / mAcm ⁻²
Initial Conditioning	H ₂	2.0	Air	2.0	100	100	50	50	80	500
Cathode Starvation	H ₂	2.0	Air	0.0/2.0	100	100	50	50	80	500
Oxygen polar	H ₂	2.0	O ₂	10.0	100	100	50	50	80	50-2000
Air polar	H ₂	2.0	Air	2.0	100	100	50	50	80	50-2000
Cathode CV (CO and H ₂)	H ₂	N/A	N ₂ – N ₂ -CO	N/A	100	100	50	50	80	N/A

Electrochemical catalyst surface area (ECSA) in MEA

The electrochemical surface area was measured by the carbon monoxide (CO) stripping method using the cell in half cell mode. Under this mode the anode electrode acts as a pseudo reference electrode. The cathode voltage was controlled at 0.125 V at 80°C and 50 kPa_{gauge} whilst purging with 1% CO in N₂ at 300 mL/min for 15 min. Afterwards the cathode was purged with N₂ at the same flow rate and for 2h to ensure that CO was removed from the bubblers and the catalyst layer pores. The adsorbed CO was oxidised electrochemically by scanning the cathode voltage from 0.125 V to 0.85 V and back to 0.05 V, at 20 mV/s, for three cycles. The area under the CO oxidation peak was integrated by subtracting the third scan from the first scan and using 420 μC/cm² constant for a CO monolayer on Pt.

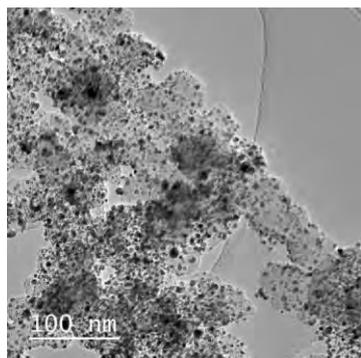
Stability protocol in 6 cm² cells

The cathode catalysts used in this work were tested for stability by using linear sweep voltammetry (LSV) under H₂/N₂ and between (0.6 – 0.925) V for a total of 30,000 cycles, at 80°C, 100% RH and ambient pressure at the cell outlet. The catalyst surface area was measured via the adsorption of carbon monoxide, at the beginning of the test, after 5,000 cycles and at the end of the test. The catalyst mass activity was monitored at the beginning of life and every 5,000 cycles until the end of the test and using a cathode starvation step before running the H₂/O₂ polarisation curve, as specified in the US-DOE Tech Team fuel cell polarisation protocol.

3. RESULTS AND DISCUSSION

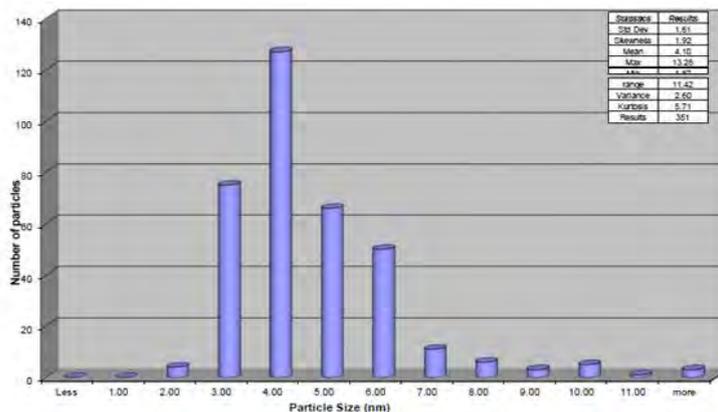
3.1 CHARACTERISATION FOR Pt/C BENCHMARK AND DEALLOYED PtNi/C REFERENCE CATALYSTS

Figure 1 and Table 5 show the characterisation data for the Pt/C benchmark and PtNi/C reference catalysts used in this task.

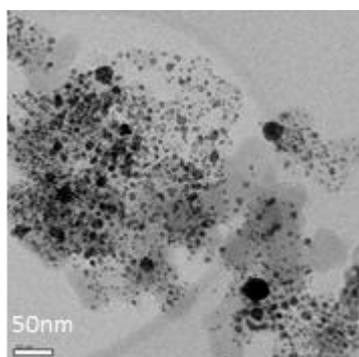


Pt/C

a)

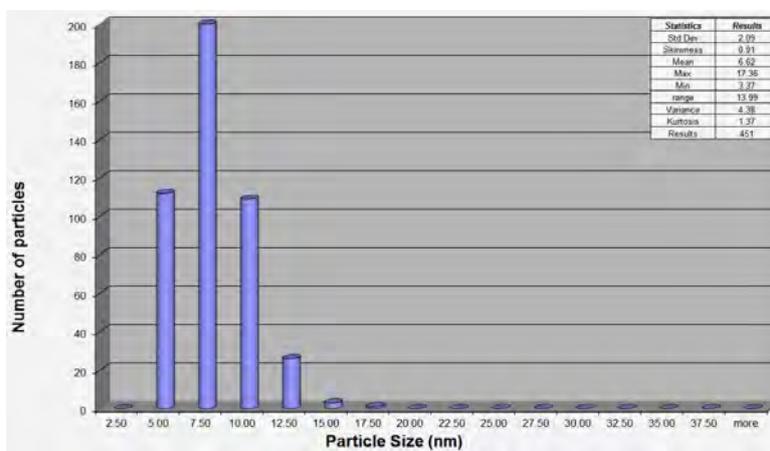


b)



PtNi/C

c)



d)

Figure 1. TEM and particle size distribution for Pt/C benchmark catalyst AA3299, Figure 1a and b. PtNi/C reference catalyst (AF9773B), Figure 1c and d.

Table 5. Characterisation data for Pt/C benchmark and PtNi/C reference catalysts.

Catalyst	Pt assay / %		Particle size (TEM) / nm	Gas phase surface area ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)	Electrochemical surface area in MEA (CO) ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)
	Pt	Ni			
Pt/C, AA3299	50.4	-	(4.1 ± 1.6) N = 351 particles	55	(55.02 ± 1.15) N = 5
PtNi/C AF9773B	28.6	4.69	(6.6 ± 2.0) N = 451 particles	46	(49.0 ± 2.8) N=3

3.2 RDE TESTING

Details of the work at TUM

TUM suggested an initial testing protocol based on prior work and recent literature⁴⁻⁷. TUM carried out experimental work on the catalyst testing, distributed the different versions of the protocol, and discussed them with the partners who provided feedback, added testing procedures *e.g.* for alloy catalysts and carbon support corrosion, and carried out experimental work to clarify open questions. Major discussion points concerned the choice of the scan rate for ORR measurements (5 mVs^{-1} or 20 mVs^{-1}), the application of the catalyst ink, and the conditions of the stability testing (potential limits, gas atmospheres). TUM also determined the temperature change of the ink when cooled in a simple water bath as compared to an ice bath during sonication.

Testing procedure for Pt-catalysts

For the Pt/C catalyst, experiments were carried out at loadings of approximately $10 \mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ and $20 \mu\text{g}_{\text{Pt}}\text{cm}^{-2}$. With the lower loading, despite the application of rotation during drying, the layers were not homogeneous, and parts of the GC electrode were uncovered. This immediately resulted in diffusion limited current densities lower than the theoretical value. At $20 \mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ both coating optical appearance and diffusion limited current densities were according to expectations. The conditioning was performed at 100 mVs^{-1} between 0.05 and 1.0 V vs RHE, for 100 cycles. The use of a low scan rate for ORR activity analysis which would not require background correction (5 mVs^{-1}) also caused problems, especially as the obtained activities did not correspond to the expectations (*cf.* also work at CNRS). Therefore a scan rate of 20 mVs^{-1} with IR-drop and background current compensation was agreed upon. The ECSA was determined after conditioning by performing three cycles in inert gas atmosphere between 0.05 and 1 V vs. RHE, and using the negative-going scan of the third cycle for analysis (*cf.* Figure 2a). The IR-drop was determined from electrochemical impedance spectroscopy. Linear sweep voltammetry between 0.05 V and 1.0 V RHE at 20 mVs^{-1} and 1600 rpm rotation rate in Ar atmosphere was used for evaluation of the background currents, and in O_2 atmosphere for ORR activity

measurement (cf. Figure 2b). The IR correction had a significant impact on the ORR current at 0.9 V vs. RHE. The background correction had a lower but non-negligible impact.

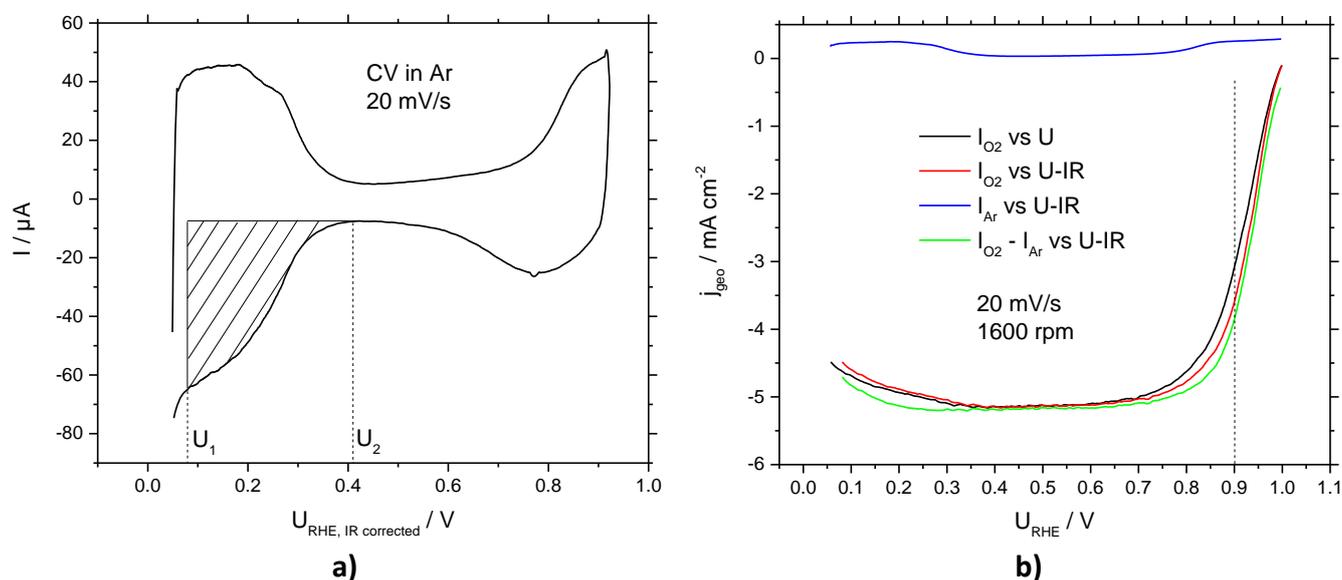


Figure 2. a) Determination of the electrochemically active surface area from cyclic voltammetry. b) Linear sweep voltammograms at 20 mV/s in Ar, IR-corrected (blue line) and O₂ as measured (black line), IR corrected (red line), and IR and background corrected (green line).

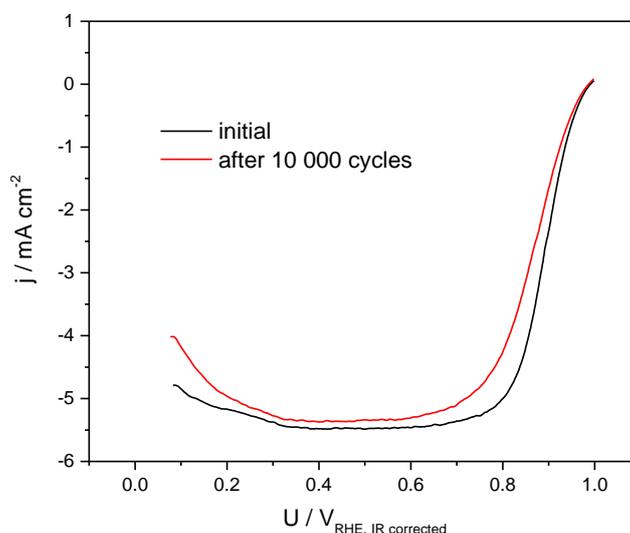


Figure 3. ORR currents measured before (black line) and after (red line) running a degradation protocol of 10,000 cycles at 100 mV/s between 0.6 and 0.925 V vs RHE in Ar, followed by conditioning.

With respect to stability testing, JM had suggested using an upper potential limit of 0.925 V, as otherwise alloy catalysts suffer an excessive activity loss that was not indicative of the losses within an actual MEA. However, cycling in oxygen environment (cf. CNRS results below) did not produce significant deterioration of the Pt catalyst. Therefore, after additional experiments mainly at CNRS, it was decided to cycle between 0.6 V and 0.925 V in inert gas atmosphere, as under these conditions the reduction of Pt oxide might be facilitated. At TUM, this protocol also resulted in a decrease in ECSA and an even stronger decrease in activity at 0.9 V after 10,000 aging cycles (cf. Figure 3).

Testing procedure for PtNi alloy catalysts

The layer fabrication was much more difficult for the PtNi alloys. In one set of experiments, an excellent-looking coating was reached using the conditions in Table 1, but the measured data showed unreasonable diffusion-limited current values, and very low activities before the degradation protocol. Often, the coating formed was not homogeneous and had to be repeated. Finally, a satisfactory coating was obtained by adding twice 10 μl of ink and drying under rotation.

As expected, the activity of the alloy catalyst clearly outperformed that of the Pt catalyst (cf. Figure 4a). The degradation protocol resulted in a decrease in ECSA and in mass activity, but did not affect the surface specific activity (cf. Figure 4b, Table 6).

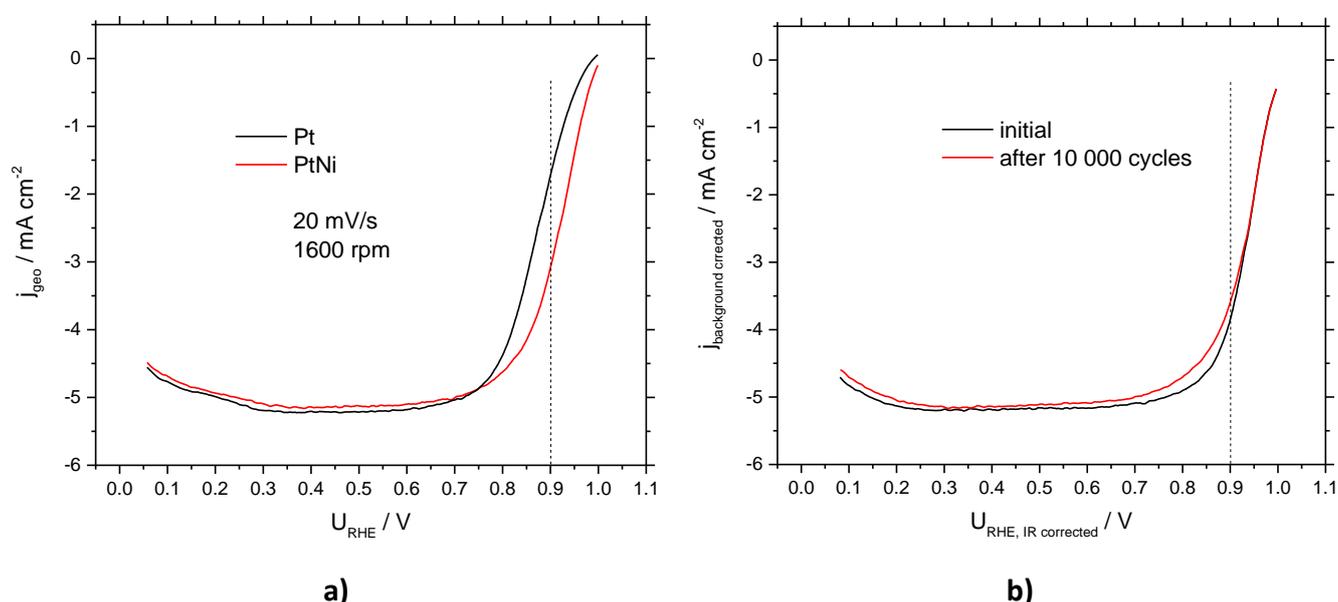


Figure 4. a) Comparison of the ORR at Pt (black) and the PtNi (red) catalyst b) comparison of the ORR at the PtNi catalyst before (black line) and after (red line) application of the degradation protocol.

Summary of Findings

The activities measured at TUM for both benchmark catalysts are summarised in Table 6.

Table 6. Benchmarking results summary of the reference Pt/C and PtNi/C catalysts (TUM).

Loading / μgcm^{-2}	Active Area / cm^2	ECSA / m^2g^{-1}	Mass activity / $\text{A mg}_{\text{Pt}}^{-1}$	Specific activity / mA cm^{-2}	Catalyst
20	2.10	53	0.75 ± 0.02	1.41 ± 0.03	PtNi/C
20	1.72	44 (-17 %)	$0.61 \pm 0,07$ (-19%)	$1,40 \pm 0,02$ (-0.7%)	Aged PtNi/C
20	2.34	59	0.24 ± 0.03	0.39 ± 0.01	Pt/C
20	2.05	52 (-12 %)	0.16 ± 0.01 (-33 %)	0.30 ± 0.02 (-23 %)	Aged Pt/C

Details of the work at CNRS

In INSPIRE WP3 Task 3.1, CNRS participated in the definition and evaluation of the catalyst screening protocol. The aim of this work was to provide a set of common procedures and electrochemical analysis practices that could minimise the data deviation among the different labs, and that could screen new supports and electrocatalysts prepared in Tasks 3.2-3.5. The screening provides relevant information on mass activity and specific activity towards oxygen reduction reaction (ORR), and relative stability when subjected to an accelerated stress test. The protocol was defined using the Pt/C reference catalyst, and the de-alloyed PtNi/C was used to evaluate the portability of the protocol.

Effects of conditioning upper potential

Usually catalysts are preconditioned before measuring the electrochemical specific surface area and the mass activity. The preconditioning step was performed to remove unwanted impurity and activate partially passivated catalyst surfaces. This preliminary step was performed by cycling the catalyst in a nitrogen saturated 0.1 M HClO₄ solution between two set voltages (0.05 to 1.0 V_{RHE} at 100 mVs⁻¹ according to the protocol) until stable voltammetric cycles were obtained. At first the effects of the upper potential limit used during the conditioning process were evaluated, comparing an electrode preconditioned at 1.0 V_{RHE} with one preconditioned at 1.2 V_{RHE}.

In Figure 5a, the stable cycle used for ECSA determination (0.05 to 1.0 or 1.2 V_{RHE} in 0.1M HClO₄ at 20 mVs⁻¹) for the reference Pt/C electrocatalyst conditioned at 1.0 V_{RHE} was compared with the one conditioned at 1.2 V_{RHE}. Larger and more defined Pt Red/Ox peaks together with a higher ECSA value of 70 m²g⁻¹ compared to 58 m²g⁻¹ were observed for the electrode preconditioned at 1.2 V_{RHE}. It is possible that the higher value measured when conditioning at 1.2 V_{RHE} could be an indication of Pt surface roughening induced by the higher upper potential. On the other hand, no effects were visible in the determination of the ORR activity where the linear scan voltammetry results obtained between 0.05 and 1.0 V_{RHE} at 20 mVs⁻¹ were matching (cf. Figure 5b). For this reason it was agreed to keep the upper potential limit as low as possible to minimise the surface modification and to avoid adopting conditioning upper potential values that would be unpractical for PtNi based catalysts.

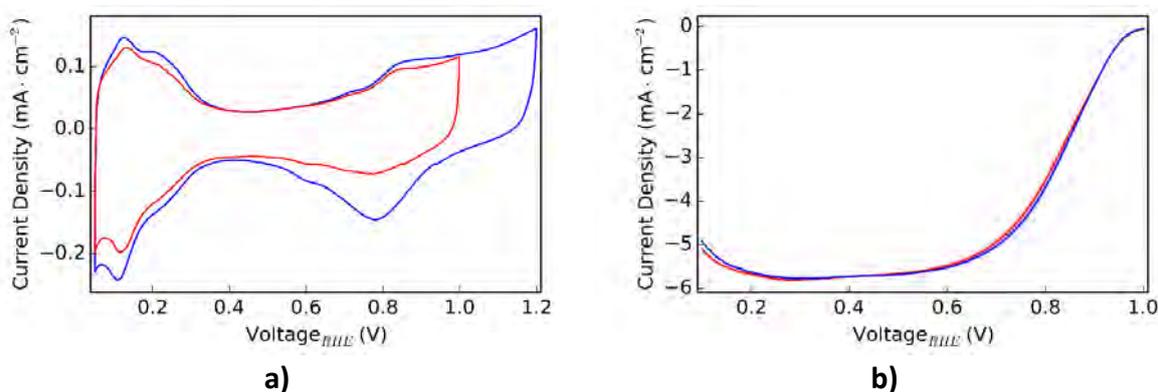


Figure 5. (a) ECSA determination and (b) oxygen reduction reaction of a Pt/C reference catalyst conditioned at 1.0 V_{RHE} (red lines) and 1.2 V_{RHE} (blue lines).

Effects of linear sweep voltammetry scan rate on the oxygen reduction reaction

Similarly to the upper potential limits in the preconditioning protocol, the effect of a key parameter in the determination of the oxygen reduction reaction behaviour of the catalyst was investigated: the linear sweep voltammetry scan rate.

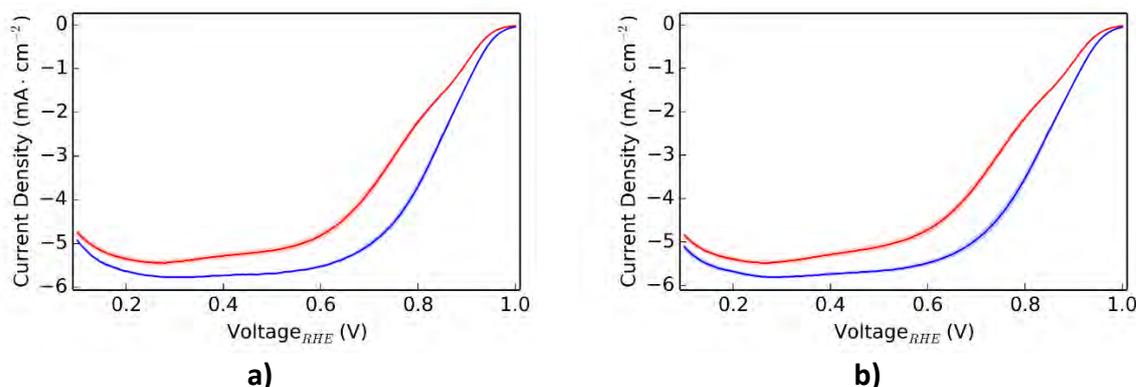


Figure 6. Oxygen reduction reaction of a Pt/C reference conditioned at (a) 1.0 V_{RHE} and (b) 1.2 V_{RHE} at 5 mVs^{-1} (red lines) and 20 mVs^{-1} (blue lines).

A reduction in scan rate from 20 mVs^{-1} to 5 mVs^{-1} induced a reduction in the estimated value of the mass activity; it has been reported that this could be the result of catalyst contamination by various elements that could be polluting the electrolyte⁸.

The numerical values of the mass activity and specific activities measured are reported in Table 7.

Table 7. Effects of the conditioning upper potential and LSV scan rate on the mass activity and specific activity of the reference Pt/C catalyst (CNRS).

Conditioning [0.05 - 1 V_{RHE}]		Conditioning [0.05 - 1.2 V_{RHE}]		LSV scan speed (mVs^{-1})
Specific Activity ($mAcm^{-2}$)	Mass Activity (Amg^{-1})	Specific Activity ($mAcm^{-2}$)	Mass Activity (Amg^{-1})	
0.30	0.17	0.24	0.17	20
0.17	0.10	0.14	0.10	5

Effects of $HClO_4$ purity on the mass activity and degradation behaviour in oxygen

An additional experiment was inspired by the large underestimation in mass activity related to electrocatalyst surface contamination by electrolyte pollution when scanning at lower rates using a standard purity Fluka TRACEselect $HClO_4$ (5 mVs^{-1} scan rate resulted in a value $\sim 40\%$ lower than obtained with 20 mVs^{-1} , Table 7). A higher purity $HClO_4$ (Ultrex II Ultrapure Reagent from JT Baker) was used in the preparation of the electrolyte. As a result the mass activity increased from 0.17 Amg^{-1} to 0.22 Amg^{-1} (30% increase); as a consequence the use of the highest possible purity is imperative in order to minimise surface contamination.

Another large effect of surface contamination was evidenced by accelerated degradation in O_2 saturated 0.1 M $HClO_4$ solution using the two different acid brands.

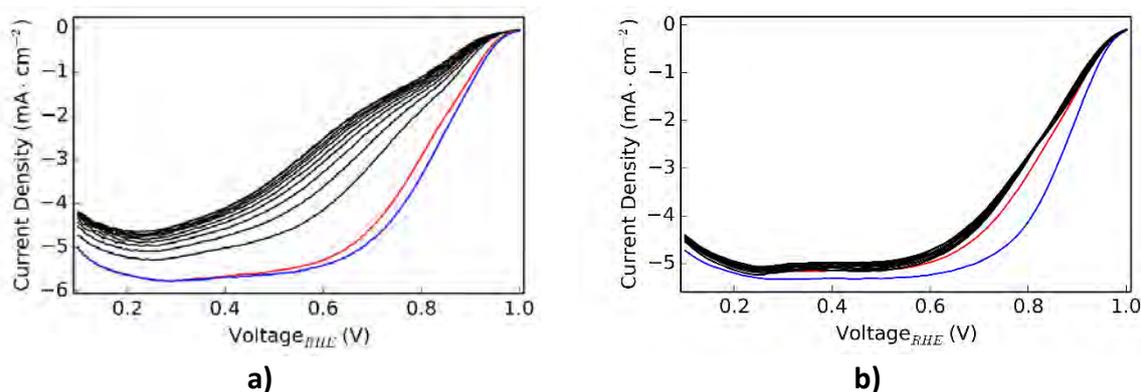


Figure 7. Oxygen reduction reaction of a Pt/C reference during degradation cycling at 100mVs^{-1} from 0.6 to 0.925 V_{RHE} in 0.1 M Fluka TRACEselect HClO_4 (a) and from 0.2 to 0.925 in 0.1M Ultrex II Ultrapure Reagent HClO_4 (b). Pristine catalyst (blue lines), reconditioned catalyst (red lines) and, during the degradation (black lines).

The same electrocatalyst showed two very distinct behaviours when using different purity electrolytes; in the Fluka TRACEselect HClO_4 most of the losses observed during the aging protocol in oxygen were recovered when the initial conditioning protocol was reapplied, indicating that most of the observed losses were related to surface contamination and not to a real degradation of the catalyst. On the other hand when a high purity reagent was used (Ultrex II Ultrapure Reagent HClO_4) the apparent catalyst degradation during cycling and the reconditioned behaviour were very similar.

Evaluation of different degradation protocols

Three different protocols were investigated: voltage cycling in an oxygen saturated 0.1 M HClO_4 solution between 0.6 and 0.925 V_{RHE} for 10,000 cycles at 100 mV/s, voltage cycling in an oxygen saturated 0.1 M HClO_4 solution between 0.2 and 0.925 V_{RHE} for 10,000 cycles at 500 mV/s and voltage cycling in an nitrogen saturated 0.1 M HClO_4 solution between 0.6 and 0.925 V_{RHE} for 10,000 cycles at 100 mV/s. The corresponding cyclic voltammograms in nitrogen and corrected linear sweeps in oxygen are reported in Figure 8.

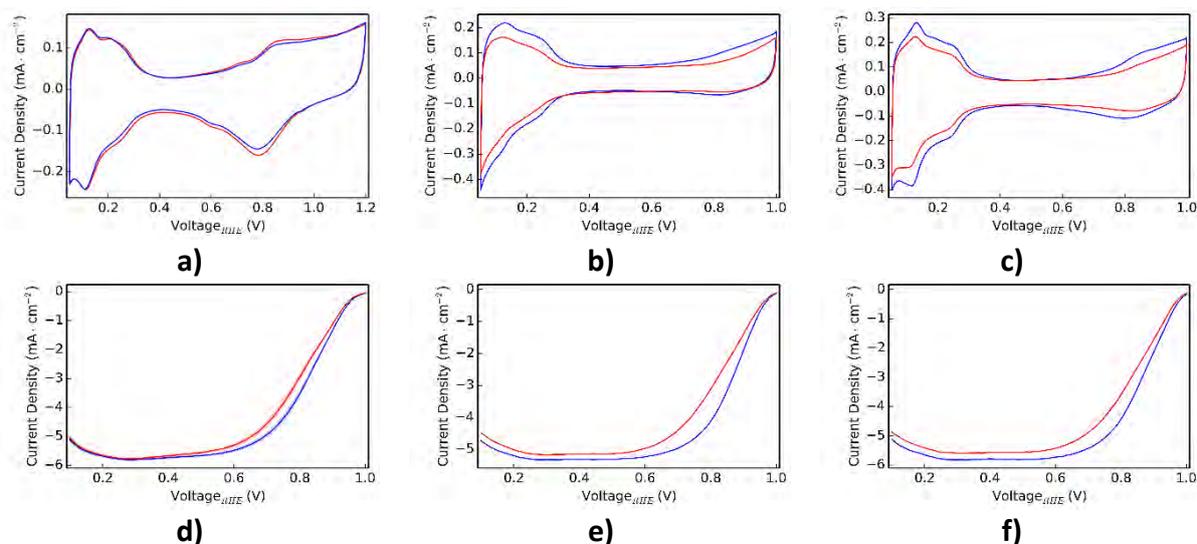


Figure 8. ECSA (a, b, c) and oxygen reduction reaction (d, e, f) of a Pt/C reference subjected to degradation cycling at 100mVs^{-1} from 0.6 to 0.925 V_{RHE} in oxygen saturated 0.1M HClO_4 (a, d), from 0.2 to 0.925 V_{RHE} in oxygen saturated 0.1M HClO_4 (b, e) and, from 0.6 to 0.925 V_{RHE} in nitrogen saturated 0.1M HClO_4 (c, f). Pristine catalyst (blue lines) and reconditioned catalyst (red lines).

The results of the different degradation protocols are compared in Table 8.

Table 8. Effects of the degradation protocol on the ECSA and mass activity of the reference Pt/C catalyst (CNRS).

Degradation protocol	ECSA variation	Mass activity loss
0.6-0.925 V_{RHE} (oxygen)	None	20 %
0.2-0.925 V_{RHE} (oxygen)	20 %	41 %
0.6-0.925 V_{RHE} (nitrogen)	20 %	23 %

Of the three different protocols, only two were found suitable because they were able to induce variation in both ECSA and mass activity and for this reason potentially able to discriminate between different catalysts: the extended range 0.2-0.925 V_{RHE} in oxygen saturated 0.1 M $HClO_4$ and the 0.6-0.925 V_{RHE} in nitrogen saturated 0.1 M $HClO_4$. Between the two the latter was chosen as nitrogen saturated media are more commonly employed in the literature.

Effects of the electrocatalyst deposited layer quality

A key factor in the determination of electrocatalytic properties of a catalyst is the quality of the deposited layer on the rotating disk electrode glassy carbon. The ink formulation, preparation and the loading of the electrode were standardised in the protocol; yet the deposition is inherently prone to variation in quality. Spin coating of the ink and static oven drying are equally regarded as valid options in the preparation of the layer and, depending on the ink properties, one or the other could be the optimal solution. The spin coating can in some cases lead to the formation of ‘coffee rings’; the formation of a thicker edge on the layer, and the static oven drying in some cases produces less uniform layers. It is then important to evaluate the quality of the layers deposited both by a preliminary optical screening and by repeating the measurement. As an example the results on two spin coated electrodes produced with the exact same protocol leading to different measured mass activity values for the Pt/C reference catalyst are described.

The catalysts shown in Figure 9 had very similar values of ECSA (59 and 61 m^2g^{-1}); the mass activity, on the other hand, shows a larger variation of 0.17 Amg^{-1} and 0.22 Amg^{-1} . This demonstrated that variation in layer quality can have measurable impacts on the oxygen reduction reaction behaviour of a catalyst.

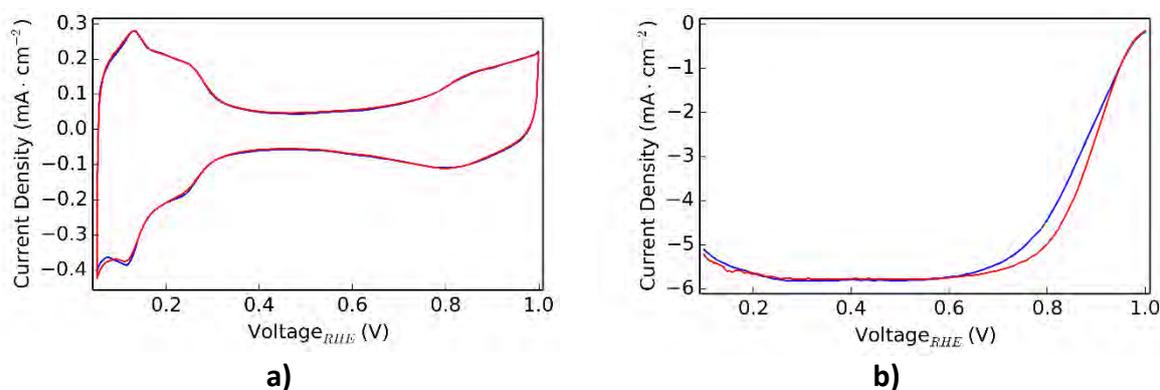


Figure 9. (a) ECSA and (b) oxygen reduction reaction of two Pt/C reference spin coated electrodes.

Reference electrocatalyst benchmarking and protocol definition

In conclusion of Task 3.1, several key parameters that could have an effect on the ex-situ electrochemical characterisation of the electrocatalysts were investigated at CNRS: the effect of the upper potential limit during the preconditioning, the effect of the linear sweep voltammetry scan rate,

the effect of the purity of the acid used in the electrolyte preparation, the effect of different accelerated stress test protocols and the effect of catalyst layer uniformity. A summary of the results is collated in Figure 10.

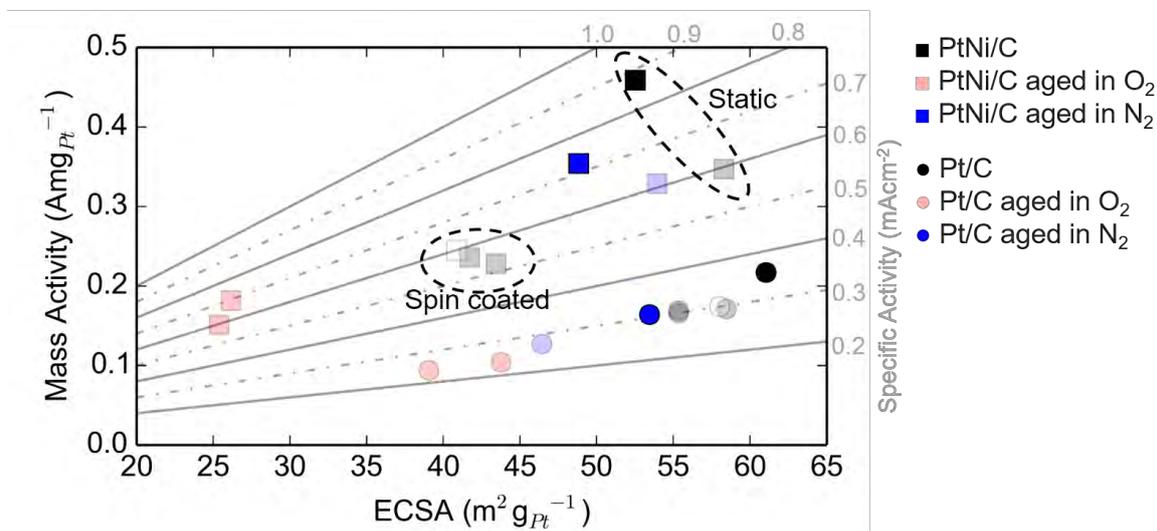


Figure 10. Protocol validation and reference catalysts benchmarking (CNRS).

Table 9. Benchmarking results summary of the reference Pt/C and PtNi/C catalysts (CNRS).

Loading / $\mu g cm^{-2}$	Active Area / cm^2	ECSA/ $m^2 g^{-1}$	Mass activity / $A mg_{Pt}^{-1}$	Specific activity / $mA cm^{-2}$	Catalyst
20	1.95	52	0.46	0.87	PtNi/C
20	1.82	48 (-7 %)	0.35 (-24 %)	0.72 (-17 %)	Aged PtNi/C
20	2.38	61	0.22	0.36	Pt/C
20	2.08	53 (-13 %)	0.16 (-27 %)	0.30 (-17 %)	Aged Pt/C

The results of the research performed by CNRS and the results obtained by the other partners made the definition of an efficient and reliable screening protocol possible. We were able to harmonise practices between several laboratories and eventually obtain consistent results. Another key result obtained was the benchmarking of the reference catalysts provided by JM summarised in Table 9.

Details of the work at TUB

The rotating disk electrode (RDE) method has been shown to be a valuable technique to screen catalysts for the oxygen reduction reaction (ORR). Relatively low amounts of catalysts are needed for the measurements and the diffusion of reactant is well defined. Many parameters are known to influence the catalyst performance. Therefore, in order to compare activity and stability of different catalysts, a generally accepted protocol within the consortium has been developed. The sections on the pre-treatment of alloys were contributed by TUB. TUB investigated several parameters to define the protocols and tested the two benchmark catalysts.

Activity

The loading of Pt on the glassy carbon electrode was investigated to select the appropriate Pt loading. Based on the formulation agreed by the consortium, a catalyst ink was prepared and drop cast onto a glassy carbon electrode (area = $0.196 cm^2$) and dried in an oven the same day that it was tested. Figure

11 shows an example of linear sweep voltammetry (LSV) for ORR activity in the case of PtNi/C. Similar curves were obtained with Pt/C. Three different loadings were tested: 10, 20 and 30 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$. The lowest loading had a problem in reaching the diffusion limited current, probably due to the difficulty in producing a closed catalyst layer with such a low loading. Both 20 and 30 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ samples showed typical LSV curves, with the latter reaching a slightly higher current magnitude at 0.9 V vs RHE. However, the mass activity would have been lower at the loading of 30 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$. The loading of 20 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ was therefore selected as optimal; also it is preferable to evaluate the activity not too close to the diffusion limiting current ¹.

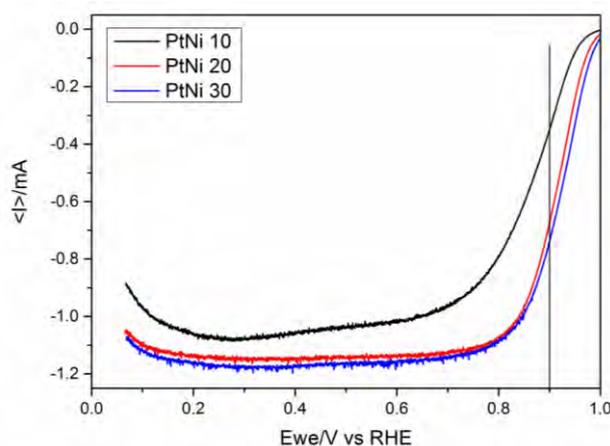


Figure 11. Pt loading study. The Pt loading for the three samples was 10 (black line), 20 (red line) and 30 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ (blue line), respectively. A vertical line intersects the curves at 0.9 V vs reversible hydrogen electrode (RHE), the potential at which the activity is estimated. Counter electrode: Pt mesh. Ref. electrode: Mercury/Mercurous Sulfate (MMS) calibrated vs RHE. Electrolyte: 0.1 M HClO_4 .

For the evaluation of the electrochemically active surface area (ECSA) two different scan rates were evaluated: 100 and 20 mVs^{-1} (Figure 12). The ECSA was derived from the hydrogen under-potential deposition region taking only the negative scan. The higher potential limit of the UPD region was easily determined by the point of lowest current in the double layer region, usually ~ 0.4 V vs RHE. The lower potential limit was taken before the onset of hydrogen evolution. This was found to be easier to evaluate at 20 mVs^{-1} , and therefore this scan rate was selected as optimal.

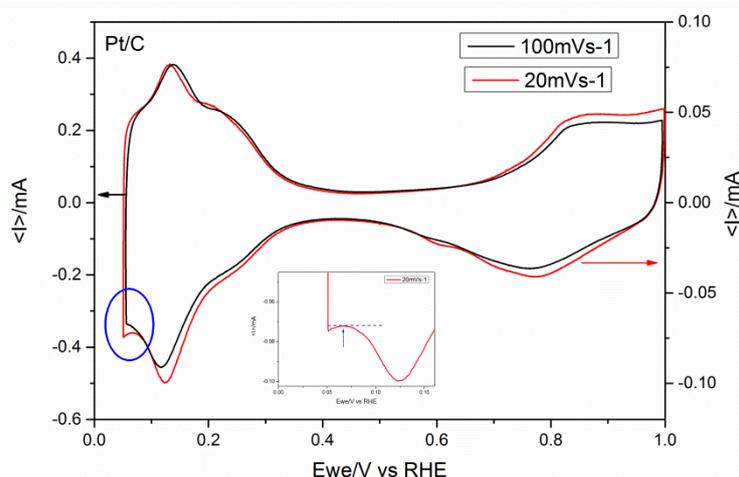


Figure 12. Scan rate and ECSA evaluation. Cyclic voltammetry at 100 mVs^{-1} (black line) and 20 mVs^{-1} (red line) of Pt/C, 20 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$. The difference at the lower potential limit is highlighted by a blue circle. The inset shows an enlargement of this region in the case of the 20 mVs^{-1} scan.

The scan rate is not only important in the determination of the ECSA but also for the evaluation of the activity. This is typically performed in O₂ saturated electrolyte by taking an anodic LSV scan. For high scan rates (typically 20 mVs⁻¹ or more) a LSV in N₂ saturated electrolyte is also performed to determine the capacitive background to be subtracted. Two different scan rates were evaluated, 5 and 20 mVs⁻¹ (Figure 13).

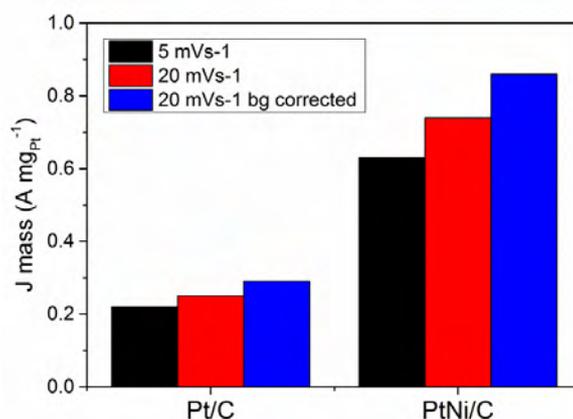


Figure 13. Mass activity at different scan rates. Mass activity at 5 mVs⁻¹ (black bars), 20 mVs⁻¹ (red bars) and 20 mVs⁻¹ with capacitive background correction (blue bars) for Pt/C and PtNi/C.

The selection of the scan rate that provides values that better resemble the real activity of the catalyst is under debate in the literature¹. The values determined using 5 mVs⁻¹ were typically lower than those obtained at 20 mVs⁻¹ (which should be considered with background correction) (see Figure 13). Together with the partners, it was agreed to use the values at 20 mVs⁻¹. At this scan rate, the catalyst should suffer less from poisoning by unavoidable impurities during the LSV, due to the faster scan rate.⁴

Stability

In order to evaluate the stability of the catalysts, different gas atmospheres (N₂ or O₂) and potential limits while cycling were investigated. The number of cycles was set as 10,000. No significant differences were found in our experiments by using O₂ or N₂ as saturation gas for the electrolytes; therefore N₂ was selected for practical reasons. The potential range was chosen in the range: 0.6 V_{RHE} - 0.925 V_{RHE}. These conditions have been judged appropriate during meetings with other partners.

Benchmarked activity and stability

Finally, JM Pt/C and PtNi/C catalysts were benchmarked with the finalised protocol. The results are reported in Table 10.

Table 10. Results of the benchmarking of activity and stability of JM Pt/C and PtNi/C with finalised protocol (TUB).

Mass normalized ECSA / m ² g _{Pt} ⁻¹	ECSA / cm ²	Mass activity / A mg _{Pt} ⁻¹	Specific activity / mA cm ⁻²	Catalyst
67.7 ± 6.9	2.89 ± 0.43	0.31 ± 0.01	0.46 ± 0.04	Pt/C
67.3 ± 9.0	2.87 ± 0.52	0.27 ± 0.01	0.40 ± 0.07	Pt/C, aged
53.2 ± 2.3	2.02 ± 0.07	0.85 ± 0.10	1.58 ± 0.12	PtNi/C
52.5 ± 0.7	1.99 ± 0.01	0.78 ± 0.15	1.49 ± 0.27	PtNi/C, aged

The initial and final activity of PtNi/C was more than two times higher than that of Pt/C. However, the ECSA of the PtNi sample was lower than the Pt one (~80%). The stability protocol produces a mild

degradation of the catalyst activity, around 10-15%, but not an appreciable decrease in the ECSA. A carbon rod will be used instead of Pt mesh as counter electrode to avoid possible Pt corrosion and redeposition from the counter electrode in future experiments.

Comparison of the results

The values obtained for the Pt/C catalysts by the different partners were comparable (cf. Table 11). Between TUM and CNRS, where the coating was applied under rotation, the agreement was excellent, while at TUB, where the coating was dried in an oven without rotation, slightly higher activities were obtained. For PtNi, all partners determined similar ECSA values. At TUM and TUB, the activity values were very similar, while the values obtained at CNRS were lower. However, for PtNi/C there was the problem of obtaining good layers. At CNRS the composition of the ink had been adjusted in order to improve the coating properties.

Table 11. Comparison of RDE results of TUM, CNRS and TUB for the Pt/C catalyst.

Loading / μgcm^{-2}	Active Area / cm^2	ECSA/ m^2g^{-1}	Mass activity / $\text{Amg}_{\text{Pt}}^{-1}$	Specific activity / mAcm^{-2}	Catalyst	Partner
20	2.34	59	0.24	0.39	Pt/C	TUM
20	2.05	52 (-12 %)	0.16 (-33 %)	0.30 (-23 %)	Aged Pt/C	TUM
20	2.38	61	0.22	0.36	Pt/C	CNRS
20	2.08	53 (-13 %)	0.16 (-27 %)	0.30 (-17 %)	Aged Pt/C	CNRS
20	2.89	67.7	0.31	0.46	Pt/C	TUB
20	2.87	67.3	0.27 (-13%)	0.40 (-15%)	Aged Pt/C	TUB

Table 12. Comparison of RDE results of TUM, CNRS and TUB for the PtNi/C catalyst.

Loading / μgcm^{-2}	Active Area / cm^2	ECSA/ m^2g^{-1}	Mass activity / $\text{Amg}_{\text{Pt}}^{-1}$	Specific activity / mAcm^{-2}	Catalyst	Partner
20	2.10	53	0.75	1.41	PtNi/C	TUM
20	1.72	44 (-17 %)	0.61 (-19%)	1.40 (-0.7%)	Aged PtNi/C	TUM
20	1.95	52	0.46	0.87	PtNi/C	CNRS
20	1.82	48 (-7 %)	0.35 (-24 %)	0.72 (-17 %)	Aged PtNi/C	CNRS
20	2.02	53.2	0.85	1.58	PtNi/C	TUB
20	1.99	52.5	0.78 (-8%)	1.49 (-5.7%)	Aged PtNi/C	TUB

3.3 CHARACTERISATION WITH THE FLOATING ELECTRODE TECHNIQUE

Measurements using the floating electrode technique were carried out at JM. Two co-workers from TUM and TUB visited JM to learn the technique and to help in carrying out the measurements. The measurements are based on the work of Zalitis et al¹⁰. In this technique the ink is applied onto a porous Au coated polycarbonate membrane that floats on the electrolyte. The oxygen gas can reach the catalyst directly through the pores of the membrane from the gas phase, therefore enhancing mass transport by several orders of magnitude, compared to the RDE. Both the Pt/C and the PtNi/C catalyst were tested. The activity at 0.9 V can be directly taken from the measured data (after IR correction) without the need for a mass transport correction. Another benefit of the method is that activity values can also be determined for potentials more relevant for actual fuel cell operation.

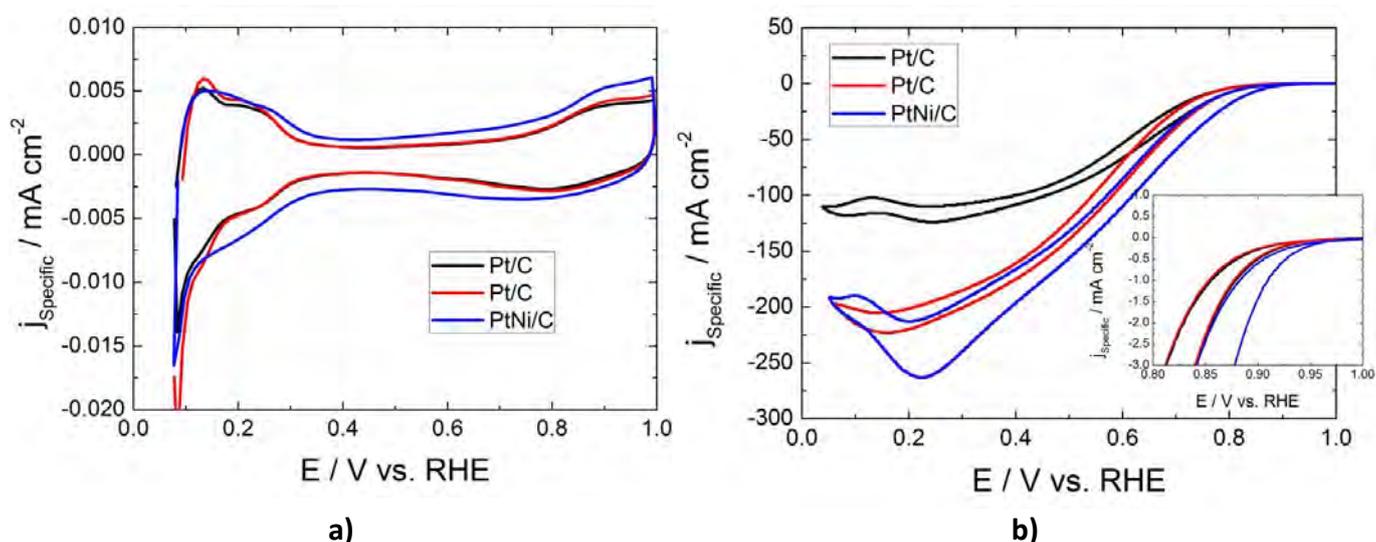


Figure 14. a) Cyclic voltammograms in nitrogen atmosphere for ECSA determination. From the determined surface area and the known specific surface of the catalyst, the mass loading of the electrode can be calculated. b) Example voltammograms for ORR at Pt/C and PtNi/C are shown.

The data were measured at 10 mVs^{-1} in 1.6 M HClO_4 . Cyclic voltammograms measured in an inert gas atmosphere for ECSA determination, and in an oxygen atmosphere for ORR activity measurement, are shown in Figure 14. For the ORR measurements, two protocols differing in the applied lower potential limit, namely 0.3 V vs. RHE or 0.0 V vs. RHE, were used. In nearly all cases, the lower limit of 0.0 V resulted in higher activity values. For Pt/C, the obtained mass and specific activities at 0.9 V (cf. Table 13) are close to those obtained in RDE measurements (cf. Table 11).

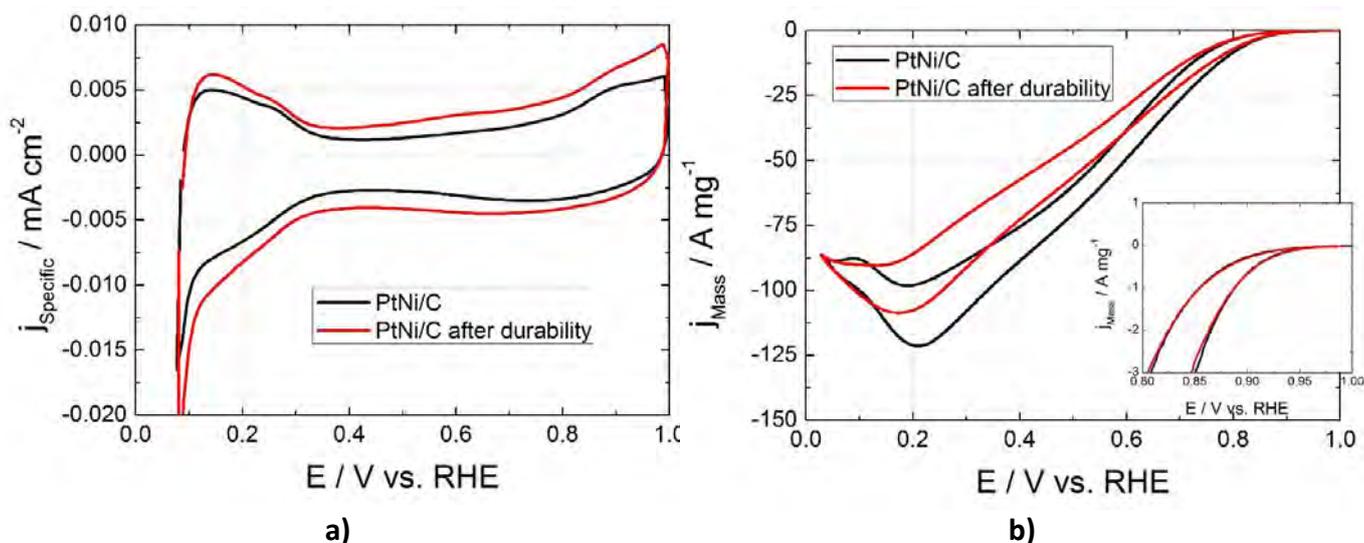


Figure 15. a) Cyclic voltammograms in nitrogen atmosphere for ECSA determination and b) voltammograms for ORR at PtNi/C before (black curves) and after (red curves) stability testing. Inset: magnified view of the high potential region.

The application of the stability protocol to the PtNi catalyst (cf. Figure 15) led to a decrease in the active surface area. While the specific activity at 0.9 V vs. RHE was increased after stability testing, there was only a small change in mass activity at 0.9 V. However, at 0.65 V vs. RHE, there was a significant loss in mass activity. This was also reflected in the activity data listed in Table 13. The mass activities at 0.9 V ranged between 0.5 and 0.7 $\text{Amg}_{\text{Pt}}^{-1}$ which was not so different from the values obtained via RDE testing (cf. Table 12). In addition, the specific activities were in the same range as some of the values found by RDE.

Table 13. Results from catalyst testing with the floating electrode technique. The data for the Pt/C catalyst marked with * was obtained after stability testing. Two different lower potential limits were applied in the ORR voltammograms, 0.3 and 0.0 V.

Catalyst	Lower Potential limit	Loading / μgcm^{-2}	Specific activity @ 0.9 V / mAcm^{-2}	Mass activity @ 0.9 V / $\text{Amg}_{\text{Pt}}^{-1}$	Specific activity @ 0.65 V / mAcm^{-2}	Mass activity @ 0.65 V / $\text{Amg}_{\text{Pt}}^{-1}$
Pt/C	0.3	5.75	0.37	0.2	38	21
Pt/C	0.0	5.75	0.49	0.27	50	28
Pt/C*	0.3	8.86	0.33	0.18	47	26
Pt/C*	0.0	8.86	0.46	0.25	64	35
PtNi/C	0.3	5.22	1.09	0.5	64	29
PtNi/C	0.0	5.22	1.44	0.66	84	40
PtNi/C	0.3	3.54	1.49	0.69	74	34
aged PtNi/C	0.0	3.54	2.08	0.65	94	30

3.4 MEA TESTING

Details of the work at JM

The catalyst mass activity was measured under H_2/O_2 , in 6 cm^2 and 50 cm^2 cells, using the US-DOE Tech Team protocol as described in the Experimental section. Figure 16 shows the mass activity plot under the descending and ascending polarisation curves.

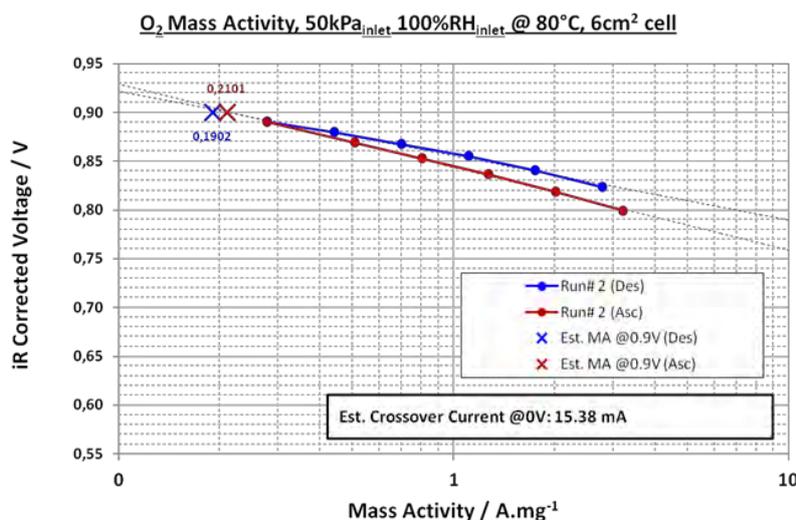


Figure 16. Mass activity plot for Pt/C benchmark catalyst in a 6 cm^2 cell.

The difference in the values is due to the amount of oxide growth on the catalyst surface. The mass activity is higher in the descending direction, from high to low current densities, i.e. from low to high voltage, which is usually attributed to less oxide being present on the Pt surface. The same protocol was applied to the PtNi/C reference catalyst and the summary of findings is shown in Table 14.

Table 14. Summary data for Pt/C benchmark and PtNi/C reference catalysts tested in 6 cm^2 MEAs. Mass activity values correspond to the descending polarisation curve as shown in Figure 16.

Catalyst	Loading / mgPtcm^{-2}	Mass activity @ 0.9 V / $\text{A}\text{mg}_{\text{Pt}}^{-1}$
Pt/C	0.20	0.21
PtNi/C	0.18	0.34

Stability testing in MEAs

Three different protocols were evaluated for stability testing in 6 cm^2 MEAs and these are summarised in Table 15.

Table 15. Stability protocols used in 6 cm^2 MEAs. Linear sweep voltammetry (LSV). Square wave (SQW).

Protocol	Electrochemical window	Sampling rate	Conditions
LSV (1)	(0.6 – 0.925) V	50 mV/s	80°C, Ambient P, H/N, 30,000 cycles
LSV (2)	(0.6 – 1.0) V	50 mV/s	80°C, Ambient P, H/N, 30,000 cycles
SQW	(0.6 - 0.925) V	3 s holds	80°C, Ambient P, H/N, 30,000 cycles

Figure 17 shows the decay in mass activity for the Pt/C benchmark catalyst using the three different protocols shown in Table 15.

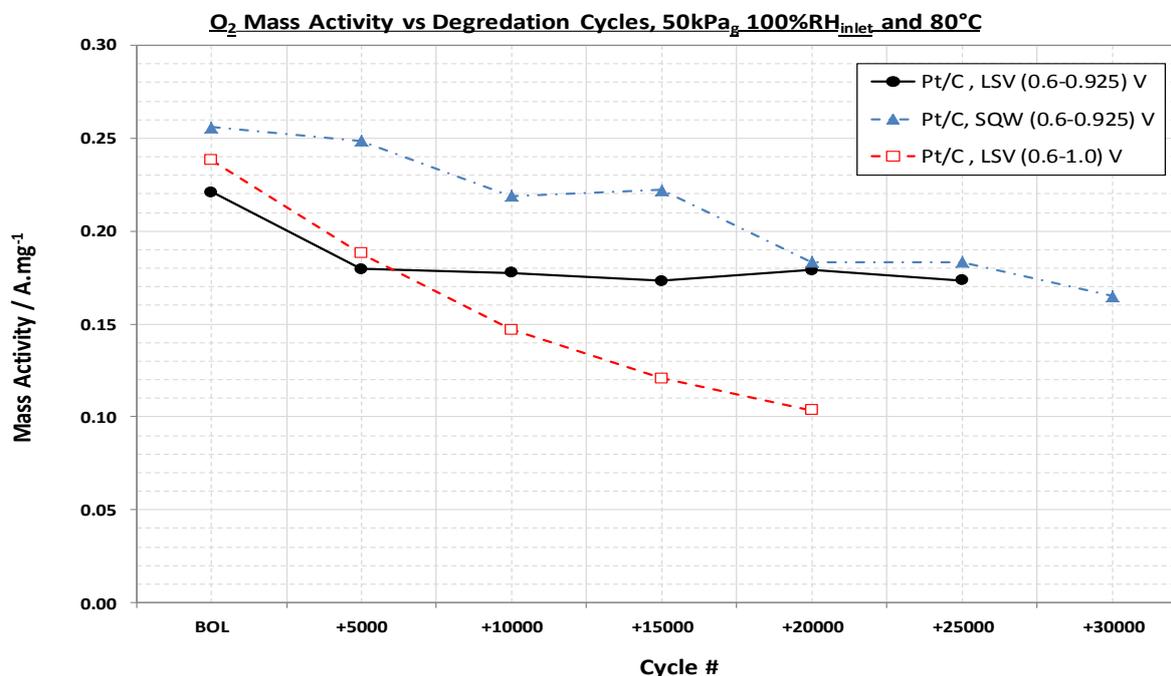


Figure 17. Mass activity decay for Pt/C benchmark catalyst under three different protocols. Linear sweep voltammetry (LSV) and square wave voltammetry (SQW).

Table 16. Summary of results for the Pt/C benchmark catalyst tested for stability using the three different protocols shown in Table 4. The Pt loading on the anode and cathode was 0.10 and 0.20 mgPtcm⁻², respectively. BOL and EOL stands for beginning of life and end of life respectively. The values between brackets show the percentage decay in surface area and mass activity after stability test.

Protocol	Electrochemical surface Area in MEA (CO) (m ² g _{Pt} ⁻¹)		O ₂ Mass Act at 0.9V / (A mg _{Pt} ⁻¹)	
	BOL	EOL	BOL	EOL
LSV, (0.6 – 0.925) V	56.01	39.93 (-29%)	0.22	0.17 (-23%)
LSV, (0.6 – 1.0) V	50.5	20.30 (60%)	0.23	0.10 (-57%)
SQW, (0.6 – 0.925) V	60.1	27.97 (-54%)	0.26	0.16 (-39%)

Results show that the LSV protocol with the higher anodic limit (0.6-1.0) V was significantly more aggressive than LSV (0.6-0.925) V. As shown in Table 16, the catalyst surface area decreased 60% and the loss of mass activity was 57% when the catalyst was cycled up to 1.0 V. The use of the square wave protocol (SQW) led to a faster decay in catalyst surface area and mass activity. In this protocol the

electrode voltage was held at 0.6V and 0.925V for 3 seconds at each voltage and the switch between these two values occurred in ~ 0.5 s. This protocol built and removed an oxide layer over the platinum surface at a much faster rate than the LSV(1) protocol. This fast oxidation and reduction of the oxide layer led to a faster degradation of the catalyst and carbon support.

Protocol LSV(1) (0.6 – 0.925) V was not as aggressive as the other two but was sufficient to show clear differences between catalyst formulations. In addition, the upper voltage limit is closer to (but higher than) the value expected to be realised in the automotive fuel cell hardware. Therefore, this protocol was adopted for screening cathode catalyst cyclic stability in WP3.

Stability testing in 6 cm² and 50 cm² MEAs with Pt/C benchmark and PtNi/C reference alloy catalysts.

The PtNi/C reference catalyst was tested in 6 cm² cells for stability using protocol LSV(1) and the results are shown in Figure 18 together with the performance of the Pt/C benchmark catalyst.

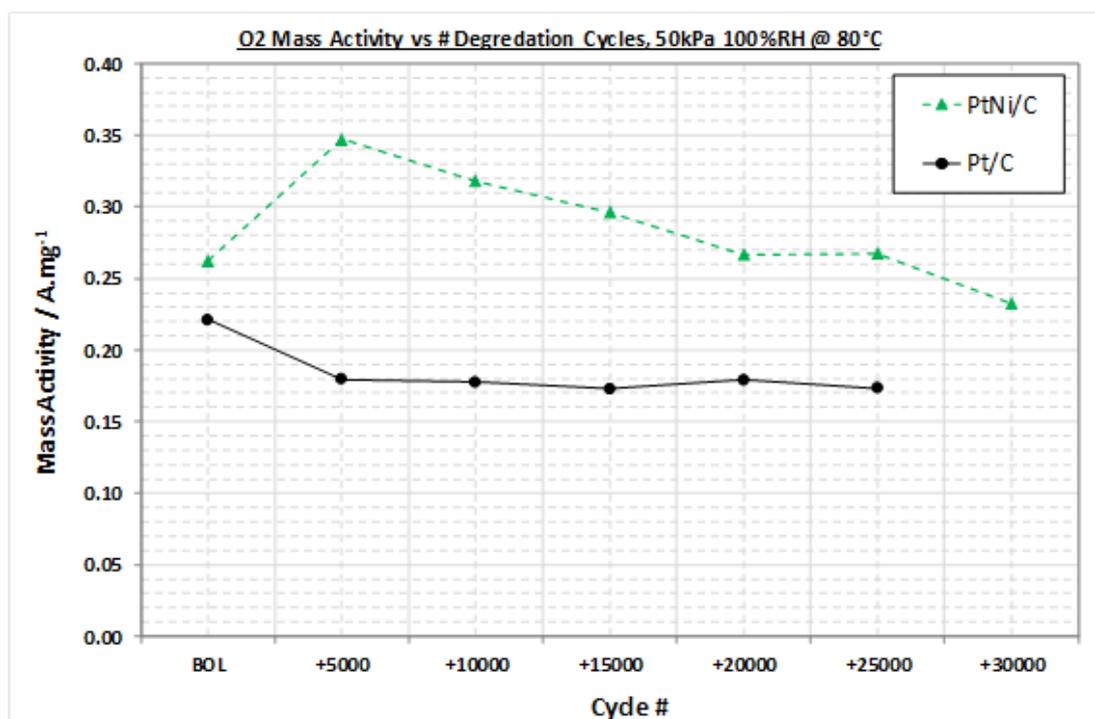


Figure 18. Mass activity decay for Pt/C benchmark and PtNi/C reference catalysts in 6 cm² cells under protocol LSV(1) (0.6-0.925)V.

Table 17. Summary of results after applying stability protocol LSV(1) (0.6-0.925) V in 6 cm² MEAs. BOL and EOL stands for beginning of life and end of life respectively. The values between brackets show the percentage decay in surface area and mass activity after stability test.

Catalyst	Electrochemical surface Area in MEA (CO) (m ² g _{Pt} ⁻¹)		O ₂ Mass Act at 0.9V / (A mg _{Pt} ⁻¹)	
	BOL	EOL	BOL	EOL
Pt/C	56.01	39.93 (-29%)	0.22	0.17 (-23%)
PtNi/C	45.87	32.95 (-28%)	0.26	0.23 (-12%)

Results show that the PtNi/C reference catalyst out-performed Pt/C in terms of loss of surface area and mass activity before and after stability testing (cf. Table 17). Therefore, it was decided to validate this positive result in 50 cm² MEAs and results are shown in Figure 19.

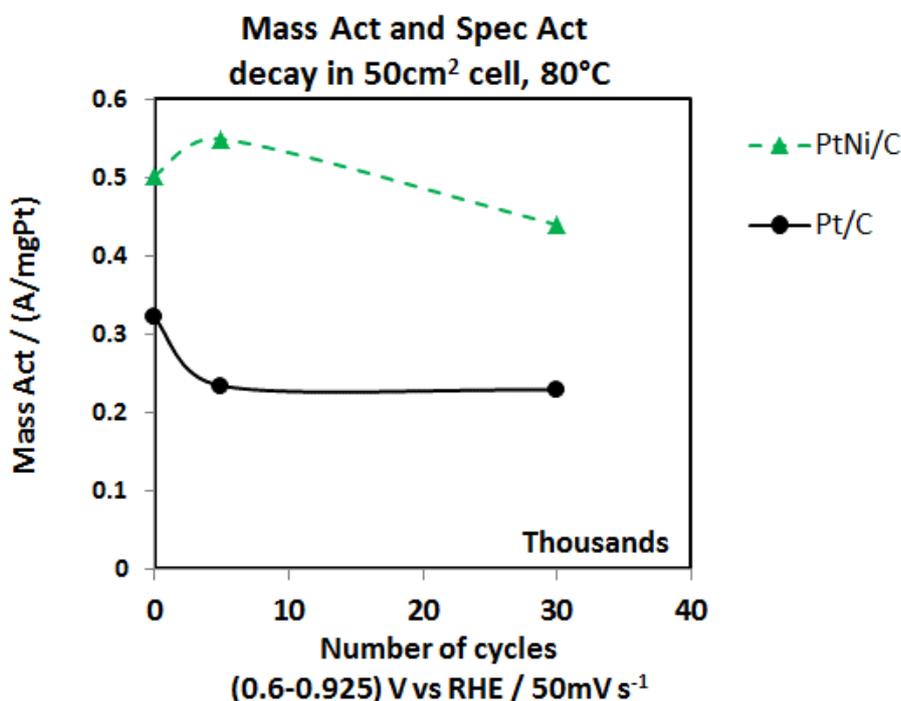


Figure 19. Mass activity decay for Pt/C benchmark and PtNi/C reference catalysts in 50cm² cells under protocol LSV(1) (0.6-0.925)V.

Table 18. Summary of results after applying stability protocol LSV(1) (0.6-0.925) V in 50 cm² MEAs. BOL and EOL stands for beginning of life and end of life respectively. The values between brackets show the percentage decay in surface area and mass activity after stability test.

Catalyst	Loading / mgPtcm ⁻²	Electrochemical surface Area in MEA (CO) (m ² g _{Pt} ⁻¹)		O ₂ Mass Act at 0.9V / (Amg _{Pt} ⁻¹)	
		BOL	EOL	BOL	EOL
Pt/C	0.20	58	32 (-45%)	0.32	0.23 (-28%)
PtNi/C	0.18	45.89	33.0 (-28%)	0.50	0.44 (-12%)

The PtNi/C reference catalyst also out-performed the Pt/C benchmark catalyst in 50 cm² MEAs (cf. Table 18). This result confirmed that the de-alloyed PtNi/C catalyst used in this work is kinetically more active than the Pt/C and retains more of its activity after the stability protocol.

4. CONCLUSIONS

Testing protocols for catalyst activity and stability measurements have been developed and validated for techniques using both the RDE and in-cell MEAs. The application of the protocol to the Pt benchmark catalyst resulted in activity values that were comparable between the different laboratories. In addition, the values were consistent with results from the floating electrode technique and even from MEA measurements. The stability protocol used a lower (less positive) upper limit than has often been used previously, reflecting the fact that in real automotive fuel cell systems that upper voltage experienced by the cathode catalyst will be controlled significantly below 1.0 V, with respect to the anode. It was shown that the cycling should be performed in inert gas, as under these conditions both ECSA and mass activity decrease by the accelerated aging; cycling in the presence of oxygen is less aggressive. All laboratories observed a comparable decrease in specific activities, but the results for the mass activities showed a larger scatter. The activity results for a PtNi catalyst were less consistent between the laboratories than the Pt/C material and some showed a larger deviation from the MEA data. The trends in activity between RDE and MEA testing for Pt/C and PtNi/C were the same, however, and both techniques can be used to screen different catalyst formulations.

5. RECOMMENDATIONS AND FUTURE WORK

The procedures for RDE testing have been distributed amongst all partners, and can be used for initial screening of the catalysts developed within the INSPIRE project. The only points that need to be adjusted for each new catalyst are the actual ink formulation and the details of the coating method. This aspect will be studied in further depth for the PtNi catalyst.

Within the project, criteria regarding activity and stability relative to the benchmark catalysts have been established that permit down-selection of the catalysts. This process can be further facilitated by floating electrode measurements, to examine the behaviour at the higher over-potentials relevant to actual fuel cell operation. Catalysts will be selected based on activity and stability compared to the benchmark catalyst.

6. REFERENCES

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