

**MASS MANUFACTURE OF MEAs USING HIGH SPEED DEPOSITION PROCESSES****Grant agreement no.: 779591****Start date:** 01.01.2018 – **Duration:** 36 months**Project Coordinator:** Technische Universität Chemnitz**DELIVERABLE REPORT****D5.1 – REPORT ON SUITABLE TEST PROTOCOLS AND BASELINE TESTING**

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NATURE OF THE DELIVERABLE

R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

D5.1– SUMMARY

Keywords	Accelerated stress test development; fuel cell material benchmarking; stationary fuel cell test protocol harmonisation
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<p>Full Abstract</p>	<p>The initial Deliverable for this task, D5.1 (M12), includes the defined set of protocols and will use the compatible components earmarked in WP2 and 3 (catalyst, ionomer and membrane) to carry out a baseline testing exercise using state-of-the-art roll-to-roll manufacturing.</p> <p>The different manufacturing techniques, as are investigated in the MAMA-MEA project, are expected to affect properties such as:</p> <ul style="list-style-type: none"> • Electrode-membrane interfaces • Catalyst layer-MPL interface • Ionomer chain orientation • Electrode mass transport • Electrode water management <p>Material characterisation is planned on three levels with specific tests defined for each of them. For the initial material qualification, ex-situ component selective tests are performed. With these, not only a valid pre-selection is made, but also any change in properties that is not in disagreement with functionality is recorded. Based on these findings, the further tests are selected from standardised in-situ component selective protocols in an initial step and specifically developed ASTs in a following step. This will be reported in D5.2 (validation testing, M24). The thereby selected materials have a high probability of working well in actual systems, which will be proven within the scope of D5.3 (durability testing in stack configuration, M36).</p>
<p>Publishable Abstract (If different from above) <i>For publication on website</i></p>	

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D5.1 – DELIVERABLE TITLE

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1. INTRODUCTION

In this Deliverable, tests will be defined to assess the influence of the in MAMA-MEA selected additive layer manufacturing processes (see **D1.4, deposition techniques down selection according to industrial MEA requirements**) on lifetime, power density and sensitivity to various stressors and resulting failure modes (degradation processes). This will enable reaching the goals defined for this project.

KPIs of MAMA-MEA

- Stack capex < 350 €/kW
- Power density > 0.67 W/cm²
- Degradation < 0.25 %/1000 h
- Lifetime expectation > 20000 h

Whereas the layer requirements are assessed in **D1.1 (specification of the deposited layers, M3)**, with the respective characterisation methods being defined in **D1.3 (detailed deposition technology assessment, M8)**, which will eventually be the basis for **D2.4 (layer characterisation, M24)**, this deliverable focuses on the available test protocols, relevant for fuel cell operation.

The aim of this project is to utilise a standard bill of materials for a volume made CCM and replicate the performance using additive deposition processes capable of much higher volumes than currently possible. There are several challenges with this approach that are highlighted below. Figure 1 defines the nomenclature of the different layers within an additive layer CCM.

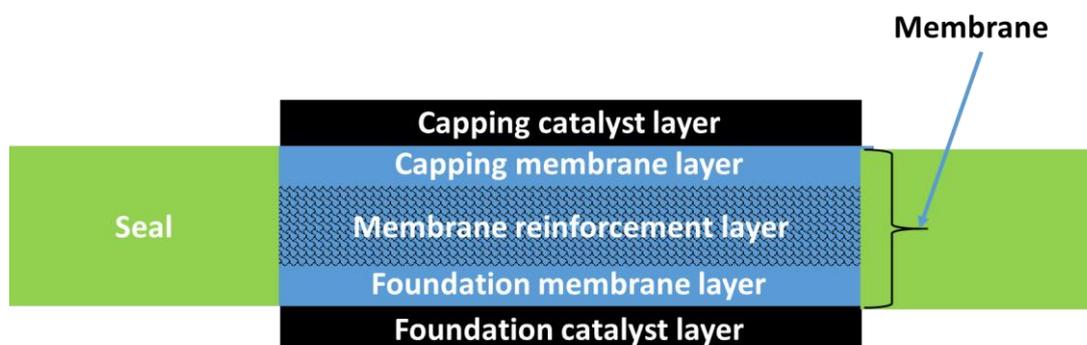


Figure 1: Schematic of additive layer CCM

The layer specific characterisation techniques serve the purpose of pre-identifying defects, but also to assess the handleability and reproducibility. These tests will give an excellent indication of properties, altered by the layer deposition method. Some of the biggest risks are changes in the catalyst layer adhesion due to altered interface properties with the membrane and inhibited mass transfer due to excessive penetration of ionomer into the porous catalyst layer structure during deposition of the membrane on top of the initial catalyst layer. The consortium is fully aware of the possibility of occurrence of these issues and – if identified in samples – has developed a plan on how to address them. Yet if no direct impact on the CCM quality is registered, minor deviations in the CL/membrane interface properties may be accepted. It must then be verified that no negative impact on the fuel cell operation is caused.



Furthermore, a blurred transition of catalytic centres to ionomer may lead to a reduction of charge transfer losses and increase the ion conductivity.

Furthermore, less explored but also a potential risk are effects of the electrode morphology on mass transport properties and water management. On the other hand, as described in the project proposal, the optimised edge architecture is expected to lead to an improved membrane swelling stability, as tension between membrane and seal are mitigated. Therefore, tests specifically aimed at humidity cycling stability are planned.

Ink composition and additives for improved handleability have been shown in preliminary experiments to cause more organic residues in the catalyst layer and thus prolong the activation time. Direct actions are not planned until an effect has been observed, but special attention will be paid to the behaviour of the materials during break in.

To ensure consistency among the fuel tests protocols used by different research groups, various test protocols¹ have been proposed. A common baseline testing based on the existing protocols (see below) will be derived. Some consortium partners have established their own test protocols. The aspects listed in Table 3 will be considered and discussed when drafting “MAMA-MEA test protocols” relevant to the Additive Layer Manufacturing Processes in the following section.

¹ For example: European- Stack-Test, EU harmonised test protocols; North America - FCTT, DOE, UNECE, FCTESTNET, FC-PAD (FC-139); China – GBZ 27753;



2. EXPERIMENTAL

SMART (specific, measurable, achievable, realistic and timely) principles are applied for efficient test design. Materials, manufactured and pre-selected in **WP 2 (technology proof of concept)** and **WP 3 (manufacturing development)** are undertaken additional ex-situ selective component tests (ESCTs) to verify their suitability in fuel cell relevant environment. This is to compliment the component testing in regard to their intrinsic properties in WP 2 and thus these tests are planned to be completed in continuous exchange and **close cooperation between JMFC, NFCT, TUC, UNIMORE and ENAS**.

Materials that pass the first iteration of testing will undergo further in-situ selective component tests (ISCTs) in accordance to available harmonised protocols, which are performed in single cell setups in full membrane-electrode-assemblies. Out of the pre-selection of tests listed below, the most relevant are chosen for the respective components. In case of indication of altered viscoelastic behaviour for example, a test protocol aimed at mechanical stress will be performed.

Only a small selection of materials will then be exposed to accelerated stress tests (ASTs). These tests are the direct link between material testing and real fuel cell operation and will again be chosen with respect to the observed material properties. In order to allow a valid comparison with other European projects and in order to comply with the **harmonisation activities of the JRC**, the **FC-DLC** will be performed on the final material selection. As there is currently no harmonised test protocol for stationary fuel cell application, the consortium has taken it upon themselves to define the relevant boundary conditions for stationary and heavy duty applications in Table 1. This has been coordinated with and communicated to the respective contacts at JRC and is planned to be implemented in upcoming further harmonised protocols.

A CCM, which is well known to the consortium and defined in **D1.1**, with a 15 μm thick reinforced membrane, a 0.08 mg/cm^2 anode and 0.4 mg/cm^2 cathode loading will be undertaken each selected test as a reference.

a.1. PREDICTED ALTERED MATERIAL PROPERTIES

The main requirement for the electrode-membrane interface is to facilitate the movement of protons across the boundary between the catalyst layer where they are produced (or consumed) and the membrane that transports them from the anode to the cathode. Therefore, the interface should have intimate contact between the ionomer network in the catalyst layer and the membrane. This however needs to be balanced with the needs of mass transport of reactants and products within the catalyst layer. In a traditional CCM manufacturing process this interface is achieved by heating the membrane to around its glass transition temperature and pressing the electrodes against its surface. This gives a good interface as the mechanical forces disrupt any skin on the membrane surface while fusing the two ionomer networks together. The degree of membrane intrusion into the catalyst layer can be controlled by the temperature and pressure used. The two electrode-membrane interfaces within an additive layer CCM will have completely different challenges and properties and will therefore be discussed separately.

a. FOUNDATION CATALYST TO FOUNDATION MEMBRANE LAYER INTERFACE

This interface is potentially the most challenging to achieve the correct properties for. This is because there is a much greater chance of negative interaction between these two layers than any other within the CCM made *via* an additive layer process. The main risk arises from the fact that the foundation catalyst layer is porous in nature, with this porosity being directly linked to the mass transport properties of the

electrode and therefore the cell performance, so the degree of penetration of the ionomer from the membrane into the catalyst layer needs to be controlled. Assessing the degree of this penetration will be an important task during this project.

b. CAPPING MEMBRANE TO CAPPING CATALYST LAYER INTERFACE

Though the membrane is non-porous there are still challenges involved in obtaining a good interface. This arises from two properties of the membrane. Firstly, the membrane structure results in it having a surface that is rich in the polymer backbone and depleted in sulphonic acid groups compared to the bulk materials. This skin needs to be disrupted by the solvent in the ink to ensure that there is good protonic connection between the membrane and catalyst layer. However, the membrane will physically swell when exposed to solvents (including water) and then contract again as the solvent dries out. This can cause cracking in the catalyst layer and therefore reduced contact area.

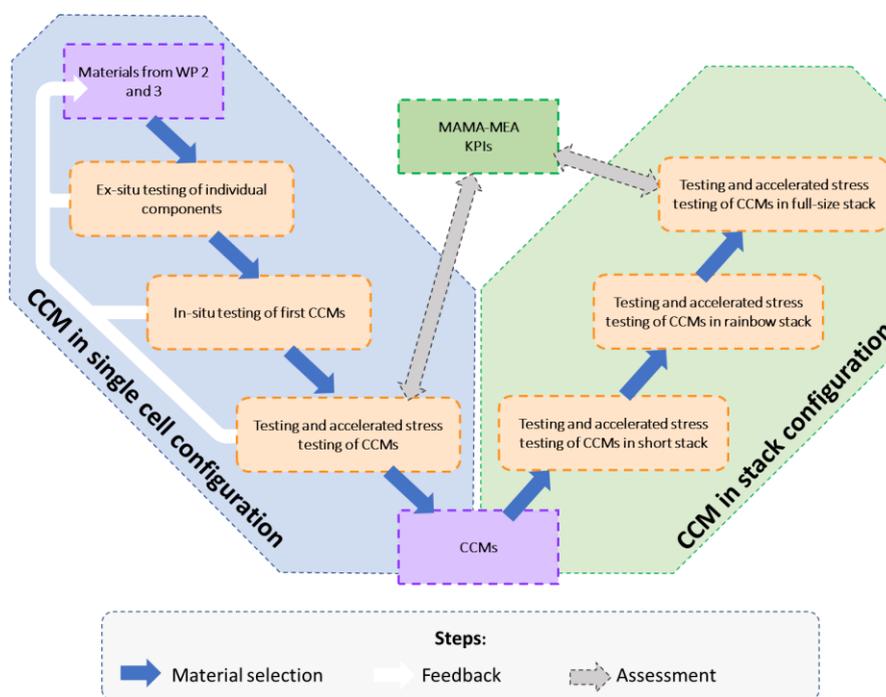


Figure 2: Flow chart of the material optimisation process

b.1. SELECTIVE COMPONENT TEST (SCT)

In order to streamline material characterisation, tests that selectively aim at specific properties are conducted. Whereas the majority of the ex-situ analyses will be covered in D2.4, a brief overview of the available approaches can be found below.

The materials that pass pre-screening are then exposed to in-situ component selective tests to thoroughly assess their fuel cell relevant operation characteristics.



c. EX-SITU TESTING

Ex-situ testing will be predominantly performed on pre-mature materials as first scanning step. Only materials that have passed these tests will be further developed into MEAs and undertaken in-situ testing. These tests are, as far as feasible, repeated with material samples, extracted from aged MEAs.

ESCT 1 – Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) is an extremely versatile and flexible analytical technique for measuring the physical properties (incl: storage modulus, glass transition temperature, etc.). The system available in JM is setup with a humidity chamber allowing to run test in close to operation condition 0-90 % RH and 20-120 °C. Several stress tests have been developed to measure the durability of membranes and CCMs. Comparisons will be made between standard CCMs and CCMs manufactured using the additive layer technique.

ESCT 2 – Catalyst layer / membrane adhesion testing

These tests are mostly covered in D2.2 and aim to be a reproducible and methodical approach to compare the catalyst layer adhesion on the membrane as well as the catalyst layer internal particle-particle adhesion.

ESCT 3 – Porosity measurement

The specific surface area of catalyst layers is determined using the **BET (Brunauer, Emmett and Teller)** method. Samples are degassed under vacuum at 90 °C for 1 hour, then 110 °C for >17 hours. Nitrogen physisorption isotherms are then measured at 77 K using a Micromeritics 3Flex analyser. Ultra-high purity N₂ (>99.9999 %) was used, with an assumed molecular cross-section of 0.162 nm². The specific surface area is determined from the BET plot over the range 0.05 to 0.3 P/P₀. This method will be applied to catalyst layers separately and also when part of a CCM. This characterisation will provide information about the ionomer catalyst interaction and if this is altered when deposited rather than laminated.

Mercury porosimetry measurements are carried out using a Micromeritics Autopore V. The pore diameter distribution is calculated using the Young-Laplace equation, with an assumed mercury surface tension of 485 dynes/cm and contact angles of 130°. Analysis of the results provides information about the porosity of the catalyst layers. It is possible to conduct this measurement on both catalyst layers and CCMs. Therefore this will be a key ex-situ test to determine if we can produce CCMs with the same structure as traditionally made parts.

ESCT 4 - Scanning electron microscope

A focused ion beam instrument (FIB) coupled with a Scanning electron microscope (SEM) can be used to slice a surface with an ion beam and image the fresh surface using software automation, this can be done in a sequential manner (slice and image) resulting in an image stack that can be used to build a three dimensional reconstruction of sample morphology. This technique allows the investigation of the interface between the membrane and the catalyst layers, as well as the pore structure of the catalyst layer.



ESCT 5 – Contact angle measurement

With the tool depicted in Figure 3, the surface hydrophobicity can be determined both in pristine samples of the individual layers as well as in aged samples. Depending on the mechanical integrity of the tested materials, the CCM will again be extracted for post-mortem analysis.



Figure 3: Setup for contact angle measurement

ESCT 6 – Optical microscopy

Optical microscopy is typically used to characterise size, shape, length, thickness and surface roughness (see appendix), and therefore enables the investigation of printing and writing process on opaque substrates and also how the ink interacts with the substrate. The optical microscope available at the institute of the TUC, a DM4000 from Leica, includes a 6-objective turret that enables up to 1000-fold magnification (Figure 4).

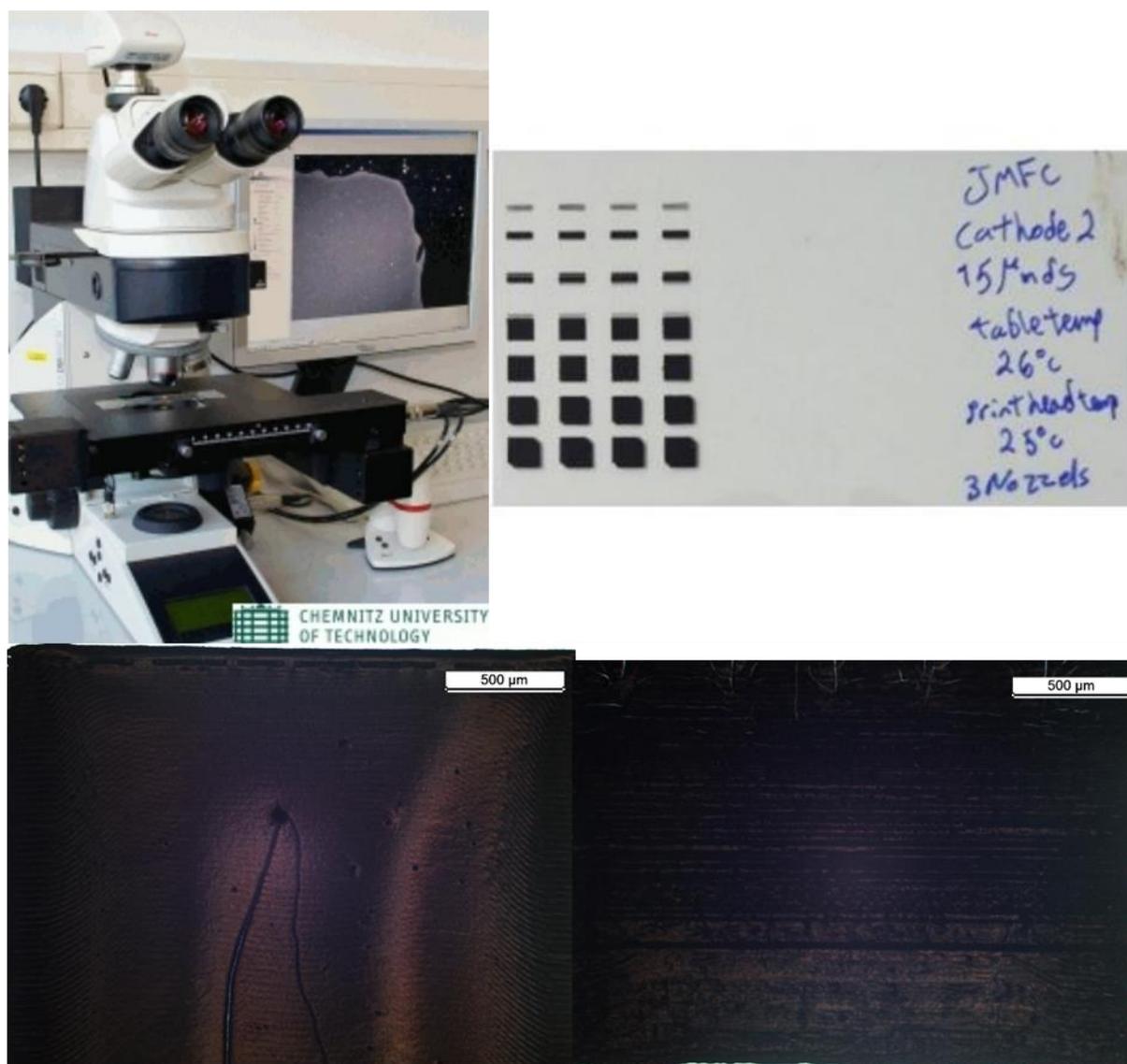


Figure 4: Optical microscope at TU Chemnitz (upper left image). Printed cathode CL samples (upper right image) and microscopic images (bottom images).

d. IN-SITU TESTING

The in-situ SCTs will be performed according to the US DoE protocols² as well internal procedures. The materials identified during ex-situ screening are further tested in full MEAs in a single cell setup in regard to their catalyst layer, carbon support and membrane stability. The two most promising sets of materials will be further undertaken the AST portraying the conditions that are expected to trigger the most likely degradation mechanism, identified during in-situ SCT.

All tests have been designed and selected based on experience, equipment availability and capacity. A potential limitation are fast switching and very high levels of humidification at high stoichiometries, as

² https://www.energy.gov/sites/prod/files/2017/11/f46/FCTT_Roadmap_Nov_2017_FINAL.pdf, accessed: 19/11/2018



they may – depending on the active area and thus flow rate – reach the limits of the respective test station humidifiers. This is avoided by completing the tests in small, single cell setups.

The Joint Research Centre (JRC) is currently developing an advanced harmonised hardware for small scale single cell measurements. This setup will allow cross-project comparison and is considered for the MAMA-MEA project if the timelines do not conflict. Until the general availability of the “JRC-test cell”, the MAMA-MEA consortium decided to use the 25-cm² balticFuelcells test cells (qCf FC25/100³) and the internal 50-cm² JMFC-test cell before using the full-size single cell based on NFCT-design. The baseline measurements were gathered using JMFC-design test cells. The 25-cm² test cell has been chosen because of faster pre-screening of the first additive-layer produced samples, to avoid a waste of materials and to ensure a good comparability with other scientific papers/works.

All test procedures will be complemented by electrochemical testing to see the impact of the stressors on the produced samples induced by the testing described below. There are numerous methods how to interpret the direct answer (potential and/or current) to conditions of a fuel cell. The potential and current are coupled – adjusting one changes the other accordingly. To interpret the impact of the additive-layer production on CCM-samples, the consortium chose these main methods: polarisation-curve measurements; electrochemical impedance spectroscopy (EIS); hydrogen-cross-over (H₂XO) measurements and electrochemical surface-area (ECSA) measurements.

The main characteristic curve of the performance depending on different load conditions of a fuel cell is a polarisation curve (Figure 5). One can directly see the overall activation losses and transport limitations of the electrochemical interfaces. It is a commonly used and easy to obtain metric for tracking a degradation of the overall fuel cell performance⁴. The partners in the consortium have multiple fuel-cell test stands to measure the polarisation curves from single cells up to full-size stacks under various conditions. Those test stands can be additionally equipped with a DC-load with potentio-/galvanostats. Those offer an additional possibility to perform, for example, better controlled cyclic voltammetry (used to obtain the ECSA⁴) or linear-sweep voltammetry (for H₂XO⁶). By additionally including a frequency response analyser, electrochemical impedance spectroscopy will be performed.

Electrochemical impedance spectroscopy (EIS) is an important technique widely used for PEMFC diagnosis and the electrochemical characterisation of PEMFC, PEMFC-materials and components⁵. It allows the characterisation of electrical properties of materials and interfaces⁶. MEAs manufactured using the additive-layer technique consist of several layers with distinct electrical properties, whose characterisation is necessary to determine the quality of the product.

EIS measurements can be performed both ex-situ and in-situ (at OCV or during operation) depending on the application. Ex-situ is the suitable approach for the characterisation of the PEMFC materials, components (e.g. CCM, BPP) and their interfaces. On the other hand, in-situ measurement is a fitting tool

³ Product of balticFuelCells GmbH more details available at <http://www.balticfuelcells.de/> (accessed 18/12/2018)

⁴ Bezmalinovic, D.; Simic, B.; Barbir, F.; Characterization of PEM fuel cell degradation by polarization change curves. *J. Power Sources* **2015**, *294*, 82–87.

⁵ Adapted for example in FCH-JU-Project HEALTH-CODE (671486) for more details visit <https://pemfc.health-code.eu/>

⁶ Zhang, J.; Zhang, H.; Wu, J.; *J. PEM Fuel Cell Testing and Diagnosis*; Elsevier, 2013. ISBN 970-0-444-53688-4



for an evaluation of the performance and the limitations of PEM single cells and PEMFC stacks (both short and full-sized).

ISCT 1 – Catalyst layer cycling stability

A square wave voltage pattern is imposed on a fuel cell, operated at 80 °C, atmospheric pressure, 4 sccm/cm² H₂ and 1.5 sccm/cm² N₂ at 100-% rH on anode and cathode, respectively. The voltage is cycled between setpoints of 0.6 and 0.95 V with 3-s hold at each step for 30.000 cycles. Electrochemical characterisation is performed periodically.

This test aims to selectively induce platinum oxidation and reduction on the cathode, accelerating catalyst agglomeration and thus loss of active surface area.

ISCT 2 – Carbon support cycling stability

The voltage is cycled in a triangular pattern between 1.0 and 1.5 V with a sweep rate of 500 mV/s for 5.000 cycles. The single cell is kept at identical conditions as in ISCT 1. Electrochemical characterisation is performed periodically.

Thereby, platinum is kept in an oxidised state, protecting the catalyst and selectively oxidising the carbon support.

ISCT 3 – Combined OCV and rH cycling

Humidity is cycled as shown in Protocol 394 in the appendix. This test operates at OCV with the RH cycled between wet and dry gases 45 s wet and 10 s dry with the membrane resistance increasing by a factor of four at the dry condition over the wet condition. The diagnostics are done every 1000 RH cycles with an OCV pressure response test to determine any leak developing. This test is heavily mechanically biased with the OCV portion having little effect.

In this test, the membrane undergoes frequent expansion and shrinkage, introducing mechanical stress. In addition, OCV conditions have been described to promote the formation of radicals and thus introducing chemical membrane degradation.

d.1. ACCELERATED STRESS TEST (AST) DEVELOPMENT

Individual, promising materials are transferred into MEAs and, depending on the identified dominant performance limitation or degradation mechanism observed in the pre-screening, exposed to specifically designed ASTs.

According to the JRC harmonised test protocol for automotive applications⁷, the boundary conditions have been adapted for stationary applications (Table 1). Any accelerated stress test should only introduce one stressor at a time either in a cyclic or continuous manner.

⁷ Tsotridis, G.; De Marco, G.; Malkow, T.; Pilenga, A. *EU harmonised test protocols for PEMFC MEA testing in single cell configuration for automotive applications*; JRC Science for Policy report: Petten, 2015.



Table 1: Proposed boundary conditions for fuel cell stressors for stationary applications.

	Parameters	Symbol	Unit	Operation conditions		
				Low Setting (L)	Reference setting (R)	High Setting (H)
Cell	Nominal cell operation temperature	T.Si.CL	°C	45	62	95
Anode	Fuel gas inlet temperature	T.Si.A	°C	RT	62	≥100
	Fuel gas inlet humidity	RH.Si.A	%	0	75	≥100
	Fuel gas inlet pressure (abs.)	p.Si.A	kPa	100	100	300
	Fuel gas composition	Conc.Si.A.H2	-	ISO 14687-2:2008		
	Fuel inlet stoichiometry	Stoic.Si.A	-	1.1	1.25	1.5
Cathode	Oxidant gas inlet temperature	T.Si.C	°C	RT	62	≥100
	Oxidant gas inlet humidity	RH.Si.C	%	0	75	≥100
	Oxidant gas inlet pressure (abs.)	p.Si.C	kPa	100	100	280
	Oxidant gas composition	Conc.Si.C.O2	-	ISO 8573-1:2010		
	Oxidant inlet stoichiometry	Stoic.Si.C	-	1.5	2.0	2.5

AST 1 – Fuel cell dynamic load cycle (FC-DLC)

This test is a translation by the JRC of the new European drive cycle to automotive fuel cell systems⁸ and used as harmonised standard in work package 5.

⁸ Tsotridis, G.; De Marco, G.; Malkow, T.; Pilenga, A. *EU harmonised test protocols for PEMFC MEA testing in single cell configuration for automotive applications*; JRC Science for Policy report: Petten, 2015.



AST 2 – Mechanical membrane and membrane-electrode interface stability

This test is taken from the US Department of Energy protocol⁹ and adapted to the operating conditions in an actual stationary application. The relative humidity is periodically (e.g. 5 min interval) varied between 0 % and 100 % on both anode and cathode during continuous short-stack or single cell operation at 0.6 A/cm² to test the mechanical stability of both the membrane and membrane-electrode interface. The test is continued for 400 h or failure of the MEA. Full BoL and EoT electrochemical characterisation, as well as MoT characterisation every 50 h is performed. MEAs in which the ohmic resistance or hydrogen cross over current changes in the range of ≥ 20 % are selected for post-mortem analysis.

This test is predominantly aiming at the mechanical integrity of the layer interfaces both between catalyst layer and membrane as well as between membrane and seal. By causing frequent expansion and shrinkage of the ionomer while in operation, a realistic failure mode is portrayed in an accelerated manner. The mechanical persistence under alternating humidity will be an important property to assess as the performance of a part for this degradation mechanism is related to its material construction and the ionomer structure within the catalyst layer. Even though the materials and composition will be the same in an additive layer CCM it is possible that the ionomer structure in the layer will be different (potential differences in thermal treatment could alter the interaction between the carbon support and the ionomer).

AST 3 – Electrode water management capabilities

The cathode relative humidity kept at >100 % (+10 % of the absolute humidity at 100 % rH) during continuous short-stack or single cell operation at 0.6 A/cm² to test the persistence of the materials under cathode flooding conditions. The test is continued for 400 h or failure of the MEA. Full BoL and EoT electrochemical characterisation, as well as MoT characterisation every 50 h is performed. MEAs in which the performance or cathode ECSA changes in the range of ≥ 20 % are selected for post-mortem analysis.

This test aims at differences in water management and persistence under over humidified conditions, as these properties are expected to potentially be influenced by the manufacturing technique.

AST 4 – Start up shut down cycling

Continuous operation at 0.6 A/cm² for 5 minutes is interrupted by switching off the load, purging the anode with air at 25 sccm/cm² for 2 minutes. For start-up, the anode is purged with hydrogen for 30 s or until OCV has been reached before turning on the load. This is repeated 1250 cycles with intermitted MoT characterisation until a performance drop of 10 % from the initial value is recorded. Conditions according to Table 1.

⁹ Benjamin, T.; Borup, R.; Garland, N.; et al. FCTT_Roadmap_Nov_2017_FINAL.pdf, 2017. Fuel Cell Technical Team Roadmap. https://www.energy.gov/sites/prod/files/2017/11/f46/FCTT_Roadmap_Nov_2017_FINAL.pdf (accessed Nov 19, 2018).

**AST 5 – Benchmarking and condition scanning standard**

The operating conditions used for the benchmark tests are shown in Table 2. This protocol was designed to test the CCM under a range of operating conditions that reflect those used in real systems. The test consists of a series of polarisation-curve measurements under different operating conditions and a temperature sweep test. In this test, the temperature of the humidifiers is held constant and the cell temperature is ramped from 50 to 90 °C; this is a stress test that gives a good finger-print for the CCM's operation.

Table 2: Protocol description for benchmark testing.

Test	Anode Gas Composition	Anode Stoich	Cathode Gas Composition	Cathode Stoich	% RHA	% RHC	Anode Inlet P (kPag)	Cathode Inlet P (kPag)	Cell Temperature (deg C)	Current Density (mAcm ⁻²)	Duration (hrs)
Initial Conditioning (Startup)	H2	1.5	Air	2	100	100	100	100	80	500	10
3-Way-Ox (100kPag)	H2	1.5	Air/Helox/O2	2.0/2.0/10	100	100	100	100	80	50-1600	
Reconditioning	H2	1.2	Air	2.5	80	80	0	0	60	500	6
2-Way-Ox	H2	1.2	Air//O2	2.5/10	80	80	0	0	60	ocv - 1600	
Reconditioning	H2	1.2	Air	2.5	80	0	0	0	60	500	6
2-Way-Ox	H2	1.2	Air//O2	2.5/10	80	0	0	0	60	ocv - 1600	
Reconditioning	H2	1.2	Air	2.5	0	30	0	0	50	500	6
2-Way-Ox	H2	1.2	Air//O2	2.5/10	0	30	0	0	50	ocv - 1600	
Reconditioning	H2	1.5	Air	2.0	100 (50 DP)	100 (50 DP)	Amb	Amb	50	1200	3
Temperature Sweep	H2	1.5	Air/O2	2.0/10.0	50DP	50DP	Amb	Amb	50-90	1200	5
100kPa Re-Conditioning	H2	1.5	Air	2	100	100	100	100	80	500	1
Cyclic Voltametry (CO CV)	H2	1.5	N2	2	100	100	100	100	80	N/A	



3. RESULTS AND DISCUSSION

Critical types of causes for so-called morphological fuel cell degradation are of mechanical nature. Those mechanical stresses can be induced/originate within the manufacturing phase and/or during the fuel cell operation. Those mechanical stressors can be induced by humidity, pressure, temperature, flooding and corresponding changes. The catalyst coated membrane (CCM) is partially protected from those changes or at least dampens their influence by the gas diffusion layer (GDL), seals, gaskets and the adjacent bipolar plates. A brief overview is provided in Table 3.

Table 3 Overview of degradation processes in the MEA¹⁰

Degradation process	Stressors
Pinhole formation in the membrane	Catalyst migration, H ₂ -crossover, radical attack, loss of F-anions
Lowering of ion-exchange capacity	Trace-metal-contamination, radical attack
Membrane ionomer delamination from membrane support (e.g. ePTFE)	rH and temperature-cycling, radical attack, mechanical stress cycling
Membrane ionomer delamination from the catalyst layer	rH and temperature-cycling, mechanical stress cycling
Membrane ionomer delamination from the seal material	rH and temperature-cycling, mechanical stress cycling, radical attack
Membrane support delamination from the seal material	rH and temperature-cycling, mechanical stress cycling, radical attack
Lowering of the water uptake capacity	radical attack, trace-metal-contamination, freeze/thaw
Perforation/shorting of the membrane	Clamping force, temperature cycling
Catalyst support conductivity reduction	radical attack
Catalysts support/ carbon corrosion	Local (over)potentials, temperature-cycling
Catalyst layer thinning	rH cycling, local overvoltages, starvations
Changes of hydrophobicity/ decrease of water management control in catalyst layer	Redistribution of ionomer
Catalyst layer cracking	rH and temperature cycling
Reduction of the catalyst's electrochemical active surface area	rH cycling – Catalyst dissolution, agglomeration, migration, de-alloying, deactivations

¹⁰ a list of used sources is in the Appendix



Catalyst- layer-ionomer recession	rH cycling
Seal material erosion; loss of elasticity	Clamping force, freeze/thaw, rH and temperature cycling
Seal cracking, displacement	Mechanical forces (e.g. vibrations)
Increasing of the mass transport resistance of reactants to and from catalytic sites	Porosity changes – mechanical, hydration, – GDL- fibre breakage, particle contamination, clamping force

One of the most likely effects of an altered electrode structure and hydrophobicity, as may occur due to the different manufacturing techniques within the MAMA-MEA project, is electrode flooding. This is predominantly an issue on the cathode, as the rH increases with current density. Under oversaturation conditions, a liquid water phase forms and hinders gas transport to the reactive sites. This is a strongly localised effect causing inhomogeneous operating conditions, as the surrounding areas are exposed to higher current densities in order to compensate the local blockage ¹¹.

On the anode, flooding induces local fuel starvation, leading to anode carbon support oxidation. Furthermore, the local void allows a higher oxygen crossover and thus the formation of a H₂/air front on the anode, which has been proven to cause cathode corrosion. Both mechanisms cause irreversible damage and are enabled by the abundance of water ¹².

This may cause:

- Higher voltage undershoot when current is increased
- Instable behaviour
- Local oxygen starvation
- Inhomogeneous current distribution
- Uneven degradation

All these effects are covered by the presented test protocols. These will be chosen depending on the predicted and in the layer characterisation step observed material properties.

To facilitate comparison, preliminary tests were performed with reference materials (Figure 5).

¹¹ Zhang, J.; Li, H.; Shi, Z.; Zhang, J. Effects of Hardware Design and Operation Conditions on PEM Fuel Cell Water Flooding. INT J GREEN ENERGY 2010, 7, 461–474.

¹² Kim, M.; Jung, N.; Eom, K.; et al. Effects of anode flooding on the performance degradation of polymer electrolyte membrane fuel cells. J. Power Sources 2014, 266, 332–340.

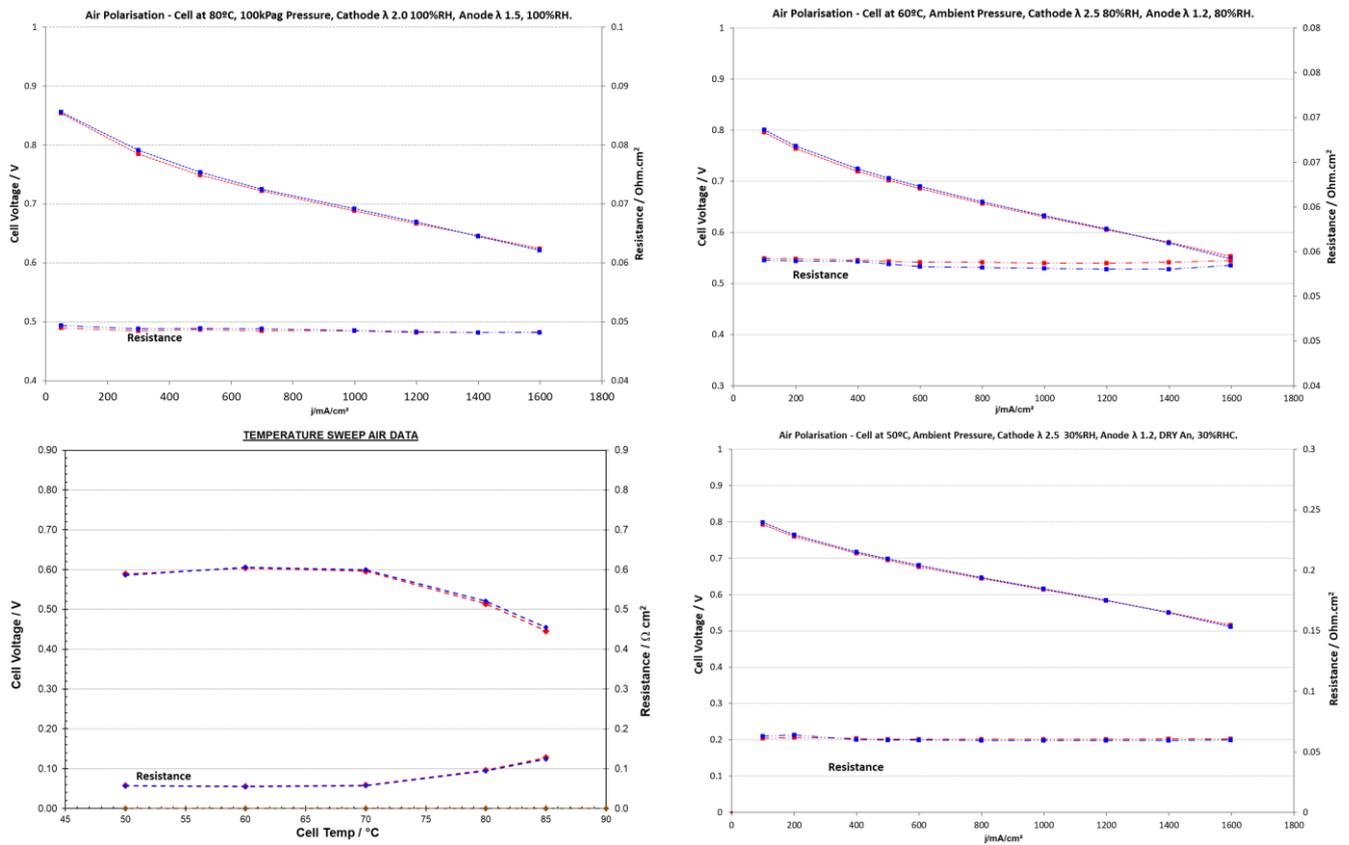


Figure 5: Upper left image: Air polarisation and resistance data for the reference CCM at 80 °C, 100 kPa_g and 100 % rH both sides. Upper right image: Air polarisation and resistance data for the reference CCM at 60 °C, ambient pressure and 80 % rH both sides. Lower left image: Air polarisation and resistance data for the reference CCM at 50 °C, ambient pressure and 30 % rH cathode and dry anode. Lower right image: Temperature sweep results showing the cell performance and resistance values at different cell temperatures while the gas humidifiers are maintained at a 50 °C dew point.



4. CONCLUSIONS

Table 4: List of addressed properties

Property focus	Ex-situ component test	In-situ component test	Accelerated stress test
Electrode-membrane interfaces	ESCT 1, 2, 3 and 4	ISCT 1 and 2	AST 1, 2 and 4
Catalyst layer-MPL interface	ESCT 1, 2, 3 and 4	ISCT 1 and 2	AST 1 and 3
Ionomer chain orientation	ESCT 1 and 5	ISCT 3	AST 2
Mass transport	ESCT 3	EC testing	AST 1 and 3
Water management	ESCT 5	ISCT 3	AST 1, 2 and 3

Material characterisation is planned on three levels with specific tests defined for each of them (Table 4). For the initial material qualification, ex-situ component selective tests are performed. With these, not only a valid pre-selection is made, but also any change in properties that is not in disagreement with functionality is recorded. Based on these findings, the further tests are selected from standardised in-situ component selective protocols in an initial step and specifically developed ASTs in a following step. This will be reported in **D5.2 (validation testing, M24)**. The thereby selected materials have a high probability of working well in actual systems, which will be proven within the scope of **D5.3 (durability testing in stack configuration, M36)**.

5. RECOMMENDATIONS AND FUTURE WORK

The results from the present deliverable will strongly correlate with **D2.4 (layer characterisation)** and will be the basis for work reported in **D5.2 (validation testing)** and **D5.3 (durability testing in stack configuration)**.

6. REFERENCES

Parsons, J. fc_42_parsons.pdf, 2009. Low Cost, Durable Seals For PEM Fuel Cells.
https://www.hydrogen.energy.gov/pdfs/review09/fc_42_parsons.pdf (accessed Nov 22, 2018).

https://www.energy.gov/sites/prod/files/2017/11/f46/FCTT_Roadmap_Nov_2017_FINAL.pdf, accessed: 19/11/2018

Product of balticFuelCells GmbH more details available at <http://www.balticfuelcells.de/> (accessed 18/12/2018)

Bezmalinovic, D.; Simic, B.; Barbir, F.; Characterization of PEM fuel cell degradation by polarization change curves. J. Power Sources 2015, 294, 82–87.



Adapted for example in FCH-JU-Project HEALTH-CODE (671486) for more details visit <https://pemfc.health-code.eu/>

Zhang, J.; Zhang, H.; Wu, J.; J. PEM Fuel Cell Testing and Diagnosis; Elsevier, 2013. ISBN 970-0-444-53688-4

Tsotridis, G.; De Marco, G.; Malkow, T.; Pilenga, A. *EU harmonised test protocols for PEMFC MEA testing in single cell configuration for automotive applications*; JRC Science for Policy report: Petten, 2015.

Benjamin, T.; Borup, R.; Garland, N.; et al. FCTT_Roadmap_Nov_2017_FINAL.pdf, 2017. Fuel Cell Technical Team Roadmap.

Zhang, J.; Li, H.; Shi, Z.; Zhang, J. Effects of Hardware Design and Operation Conditions on PEM Fuel Cell Water Flooding. *INT J GREEN ENERGY* **2010**, *7*, 461–474.

Kim, M.; Jung, N.; Eom, K.; et al. Effects of anode flooding on the performance degradation of polymer electrolyte membrane fuel cells. *J. Power Sources* **2014**, *266*, 332–340.

d.2. OVERVIEW DEGRADATION MECHANISMS

[1] Mench, M., Kumbur, E. C., Veziroglu, T. N., Eds. *Polymer Electrolyte Fuel Cell Degradation*, 1st ed.; Academic Press: Oxford, 2012.

[2] Dubau, L.; Castanheira, L.; Maillard, F.; et al. A review of PEM fuel cell durability: materials degradation, local heterogeneities of aging and possible mitigation strategies. *WIREs Energy Environ* **2014**, *3*, 540–560.

[3] Kneer, A.; Jankovic, J.; Susac, D.; et al. Correlation of Changes in Electrochemical and Structural Parameters due to Voltage Cycling Induced Degradation in PEM Fuel Cells. *J. Electrochem. Soc.* **2018**, *165*(6), F3241–F3250.

[4] Wang, C.; Zhang, J.; Wang, S.; et al. Degradation study of Membrane Electrode Assembly with PTFE/Nafion composite membrane utilizing accelerated stress technique. *International Journal of Hydrogen Energy* **2016**, *41* (36), 16212–16219.

[5] Young, A. P.; Stumper, J.; Knights, S.; Gyenge, E. Ionomer Degradation in Polymer Electrolyte Membrane Fuel Cells. *J. Electrochem. Soc.* **2010**, *157* (3), B425–B436.

[6] Wessel, S. fc049_wessel_2011_o.pdf, 2011. Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells. https://www.hydrogen.energy.gov/pdfs/review11/fc049_wessel_2011_o.pdf (accessed Dec 06, 2018).

[7] Wessel, S.; Harvey, D. fc049_wessel_2013_p.pdf, 2013. Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells. https://www.hydrogen.energy.gov/pdfs/review13/fc049_wessel_2013_p.pdf (accessed Dec 06, 2018).



[8] Lin, Ch.; Chien, Ch.; Tan, J. Chemical degradation of five elastomeric seal materials in a simulated and an accelerated PEM fuel cell environment. *J. Power Sources* **2011**, *196*, 1955–1966.

[9] de Bruijn, F. A.; Dam, V. A. T.; Janssen, J. M. Review: Durability and Degradation Issues of PEM Fuel Cell Components. *FUEL CELLS* 2008, *1*, 3–22.

[10] Yan, Q.; Toghiani, H.; Lee, Y.; et al. Effect of sub-freezing temperatures on a PEM fuel cell performance, startup and fuel cell components. *J. Power Sources* **2006**, *160*, 1242–1250.

[11] Internal know-how of partners from the MAMA-MEA consortium

7. APPENDIX

d.3. ADDITIONAL RESULTS

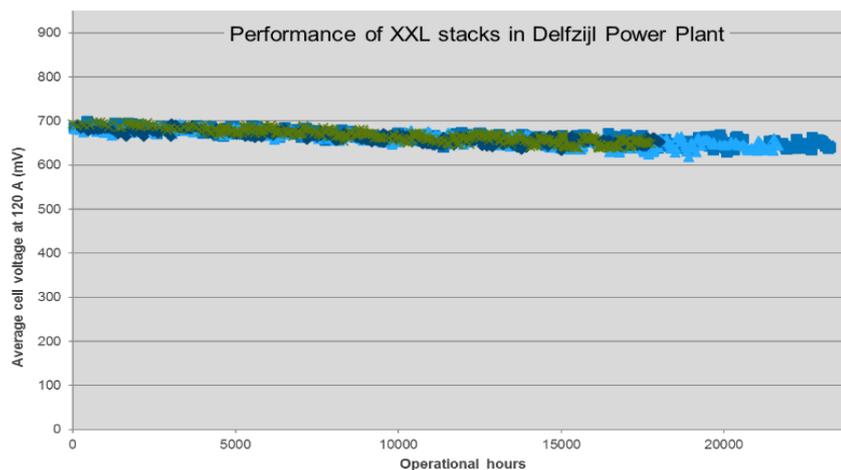


Figure 6 The results of durability tests with a 75-cell fuel cell stack featuring stabilised electrodes (intended for use in the MAMA-MEA project as a reference) show the voltage decay rate of less than 3 $\mu\text{V}/\text{h}$ over a period of over 23,000 hours.

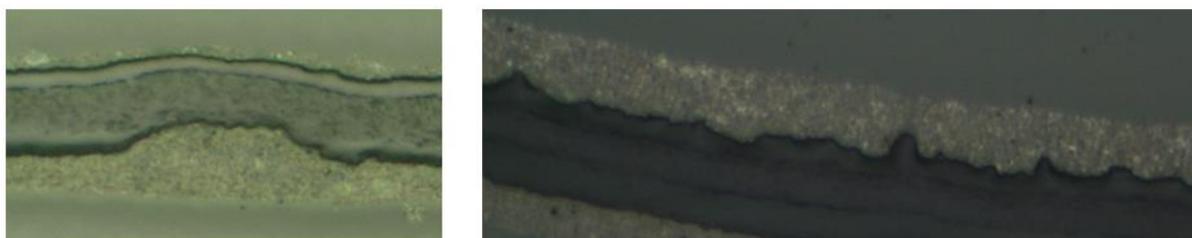
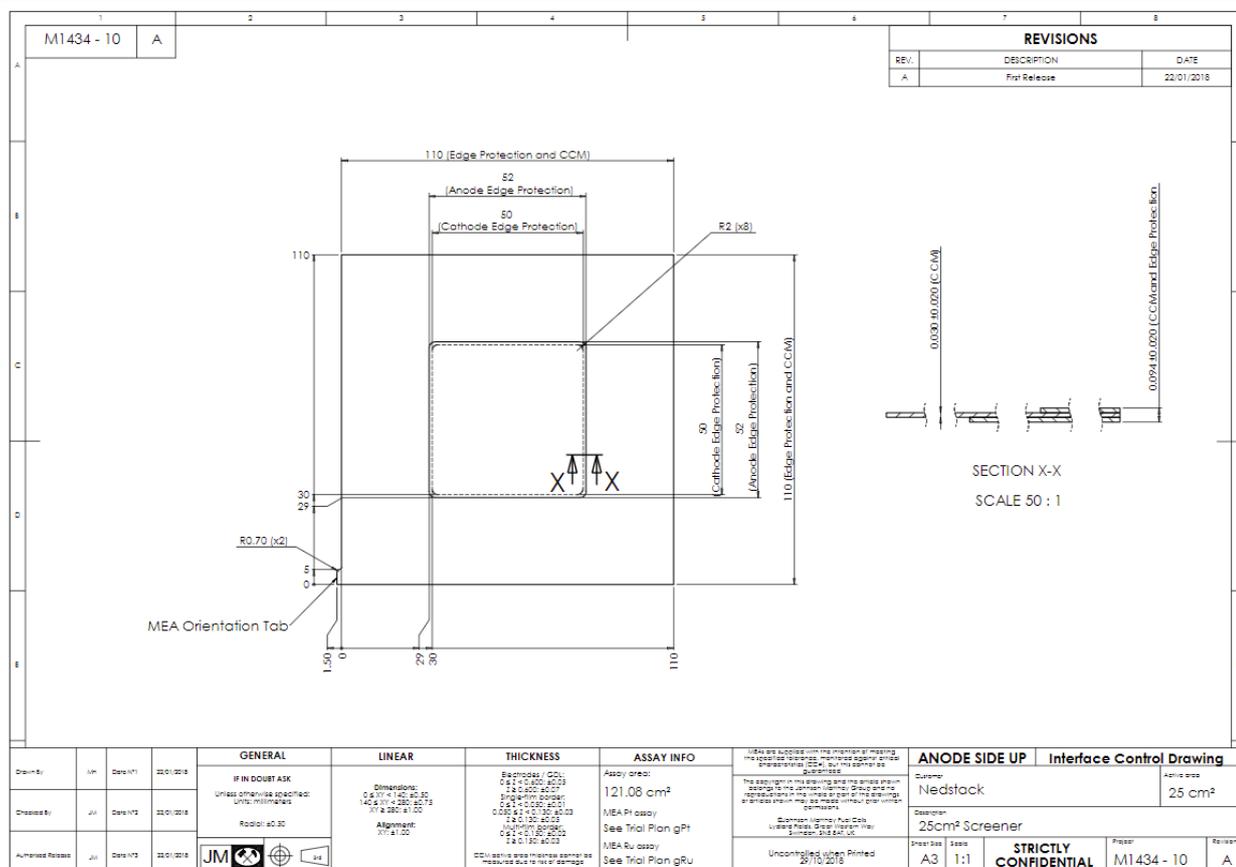


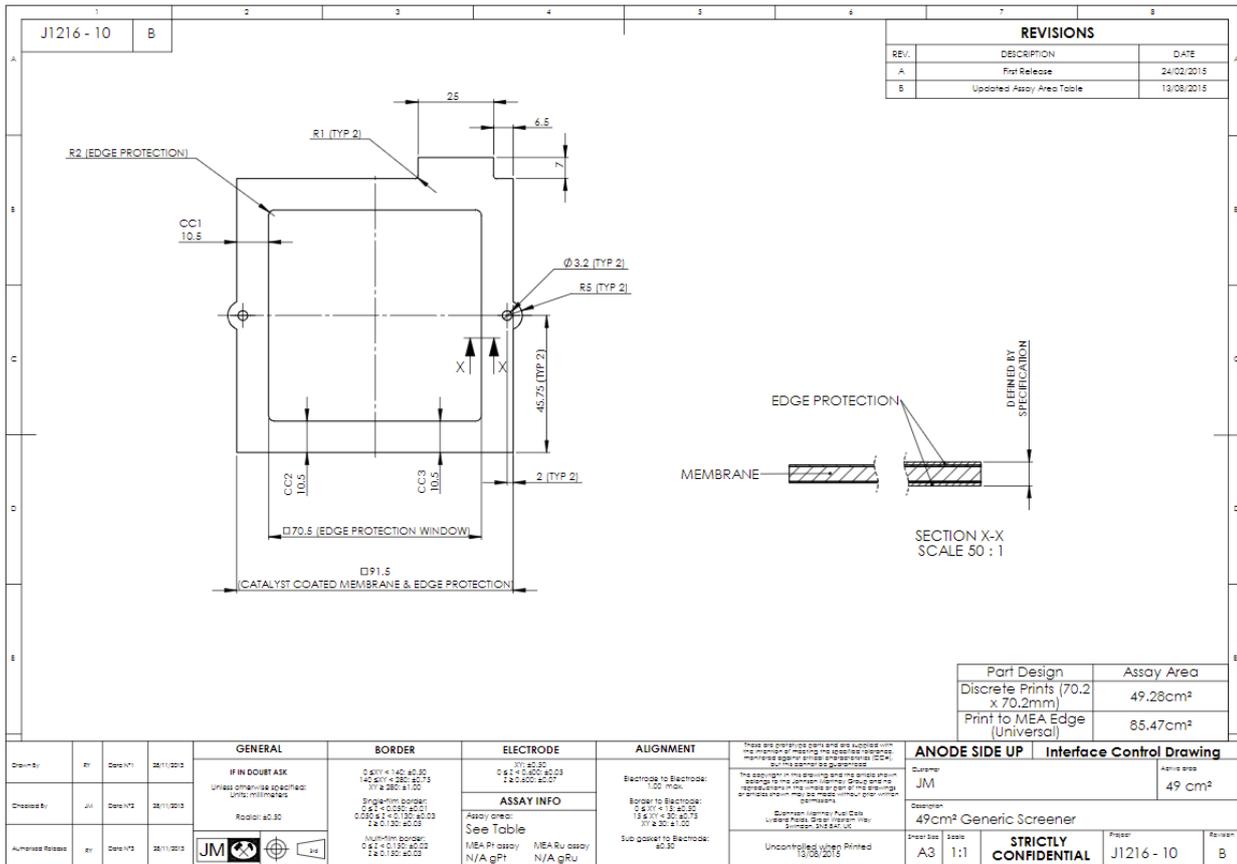
Figure 7: Examples of CCM defects; on the left: lump, on the right: crack.



d.4. GEOMETRY OF THE SAMPLES USED IN MAMA-MEA FOR THE PRELIMINARY TESTING



Drawn By	LM	Date/Ver	22/01/2018	GENERAL	LINEAR	THICKNESS	ASSAY INFO	ANODE SIDE UP	Interface Control Drawing
Checked By	JM	Date/Ver	22/01/2018	IF IN DOUBT ASK Unless otherwise specified: Units: millimeters	Dimensions: 0.5 (H) ± 0.02, 40.00 10.5 (H) ± 0.02, 50.75 17 ± 0.01 ± 0.02	Electrodes (CCM): 0.2 ± 0.005, 0.023 1.8 ± 0.005, 0.001 Single Pt anode: 0.005 ± 0.001, 0.003 0.2 ± 0.005, 0.001 0.2 ± 0.005, 0.001 0.2 ± 0.005, 0.001 1.8 ± 0.005, 0.003	Assay area: 121.08 cm ² MEA Pt assay See Trial Plan gPt MEA Ru assay See Trial Plan gRu	Current Nedstack	Area 25 cm ²
Approved/Revised	JM	Date/Ver	22/01/2018	Radius: 40.50   	Alignment: 17 ± 0.02	CCM parts and thicknesses given as measured due to tolerances	Supplier/Manufacturer/Part No. Living Media, Green Innovation, 1100 Shanghai, 201203, P.R. China	Description 25cm ² Screener	Sheet Size A3
							Uncontrolled When Printed 29/10/2018	Scale 1:1	Version A



d.5. NOMENCLATURE FOR THE MAMA-MEA PROJECT

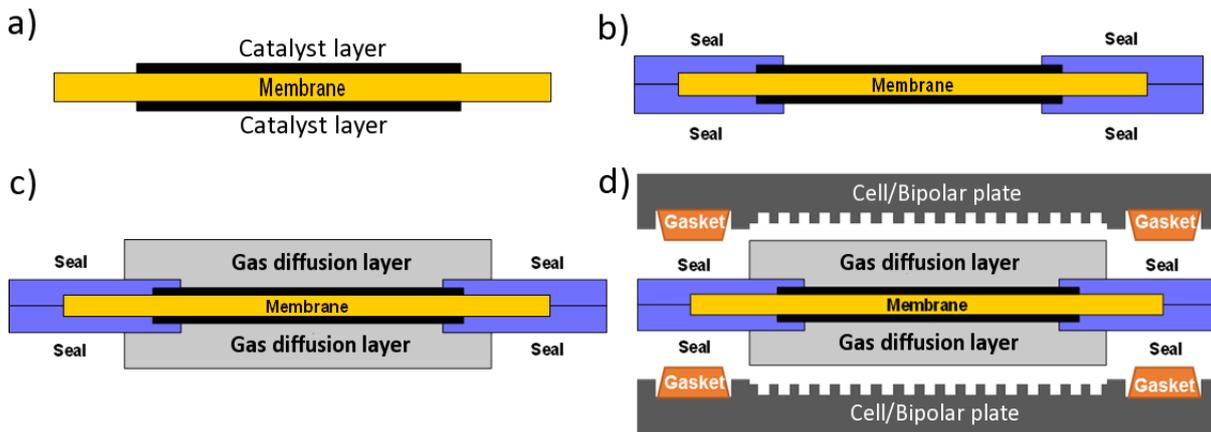


Figure 8: An illustration of CCM nomenclature used in the proposal. a) Catalyst-Coated Membrane, b) Sealed CCM, c) Membrane Electrode Assembly, d) MEA stack hardware integration.

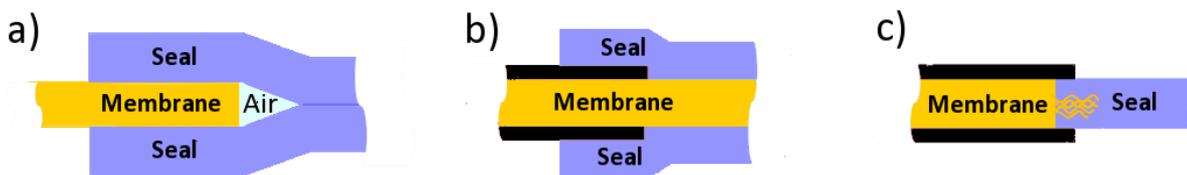


Figure 9: Edge architecture of current CCM designs with membrane and catalyst extended into seal region.



d.6. PROTOCOL 394 – COMBINED OCV / RH CYCLING MEMBRANE AST

Test	Anode Gas Composition	Anode Stoich	Cathode Gas Composition	Cathode Stoich	% RHA	% RHC	Anode Inlet P (kPag)	Cathode Inlet P (kPag)	Cell Temperature (deg C)	Current Density (mAcm ⁻²)	Duration (hrs)
Initial Conditioning (Startup)	H2	1.5	Air	2	100	100	100	100	80	500	10
Cycling Through Steps Below until 20000 cycles											
1000 RH Cycles	H2	2000sccpm	Air	2000sccpm			0	0	90	0	6
Diagnostics Step 1	N2	2000sccpm	N2	2000sccpm	100	100	0	0	90	0	2mins
Diagnostics Step 2	N/A	300sccpm	Air	2000sccpm	100	100	0	0	90	0	15mins
Diagnostics Step 3	N2	2000sccpm	N2	2000sccpm	100	100	0	0	90	0	2mins
Diagnostics Step 4	H2	2000sccpm	N/A	300sccpm	100	100	0	0	90	0	10mins
Diagnostics Step 5	H2	2000sccpm	Air	2000sccpm	100	100	0	0	90	0	2mins
Diagnostics Step 6	H2	300sccpm	Air	300sccpm	100	100	50/50/0	50/0/0	90	0	10mins
Back To 1000 RH Cycles											

Note: RH cycles - 10 s dry gas, 45 s wet gas.