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IMMORTAL

IMPROVED LIFETIME STACKS FOR HEAVY DUTY TRUCKS THROUGH ULTRA-DURABLE COMPONENTS

Grant agreement no.: 101006641

***Start date**: 01.01.2021 – **Duration**: 36 months*

***Project Coordinator**: D. J. Jones, CNRS*

DELIVERABLE REPORT

D5.3 – CHARACTERISATION OF SOA BASELINE AUTOMOTIVE COMPONENTS IN HD CONDITIONS	
Due Date	31 December 2021
Author (s)	Adam Hodgkinson , Iosif Vazirgiantzikis (JMFC)
Workpackage	5
Workpackage Leader	JMFC
Lead Beneficiary	JMFC
Date released by WP leader	30 June 2022
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DISSEMINATION LEVEL		
PU	*Public*	***X***
PP	*Restricted to other programme participants (including the Commission Services)*	
RE	*Restricted to a group specified by the consortium (including the Commission Services)*	
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NATURE OF THE DELIVERABLE		
R	*Report*	***X***
P	*Prototype*	
D	*Demonstrator*	
O	*Other*	

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SUMMARY	
Keywords	*State-of-art, MEA, AST, LPT, degradation, physical characterisation, chemical characterisation*
Abstract	*This report documents the work carried out to characterise the IMMORTAL baseline membrane electrode assembly (MEA), a state-of-the-art MEA designed for heavy-duty operation. The MEA was characterised for performance in both subscale single cell and stack operation using load profile tests (LPT). The MEA was additionally characterised by accelerated stress tests (AST) and post-mortem analysis of the catalyst layer to allow identification of degradation mechanisms from stack level load profile tests. The growth of the Pt particles appeared to occur differently in the stack LPT tests compared to the ASTs; it was, therefore, concluded that the AST could not fully predict LPT degradation.*
Public abstract for confidential deliverables	

REVISIONS			
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D5.3 – CHARACTERISATION OF SOA BASELINE AUTOMOTIVE COMPONENTS IN HD CONDITIONS

CONTENTS

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1 INTRODUCTION

This report documents the work carried out to assess and characterise the current IMMORTAL Baseline state-of-the-art (SoA) automotive membrane electrode assemblies (MEAs) under heavy-duty conditions. The beginning of life (BOL) and end of life (EOL) performance were measured on these MEAs under subscale conditions, and accelerated stress tests (ASTs) applied.

2 SCOPE

The scope of this report was to investigate the effect of Pt dissolution and carbon corrosion ASTs on the performance of the MEA at subscale, and on Pt nanoparticle size and distribution located internally/externally. Furthermore, the chemical and mechanical stability of the IMMORTAL SoA membrane were investigated.

The specific topics discussed in this report are:

- Subscale performance, ASTs (Pt dissolution and carbon corrosion) of the IMMORTAL SoA Baseline MEA.
- The effect of Pt dissolution AST on the catalyst layer internal and external Pt particle size and distribution.
- The effect of carbon corrosion AST on the catalyst layer internal and external Pt particle size and distribution.
- The chemical and mechanical stability of the IMMORTAL SoA membrane.
- Review of stack load profile test (LPT) performance as well as voltage decay during the tests.

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3 Results and Discussion

3.1 MEA Composition

The IMMORTAL Baseline MEA is based on the best of technologies from the automotive sector adapted for heavy-duty operation. The anode is a cell reversal tolerant (CRT) design with low iridium leach rate. The membrane is a 15 µm low EW ePTFE (expanded polytetrafluoroethylene) reinforced membrane with chemical stabilisation additive. The specification of the IMMORTAL Baseline MEA is summarised in Table 1, and further details are provided in D5.1.

Table 1: IMMORTAL SoA Baseline MEA Specification.

Component	Description	Notes
Cathode	0.6 mg Pt/cm^2	Low EW ionomer
Anode	0.08 mg Pt/cm^2	Cell reversal tolerant
Membrane	15 micron ePTFE reinforcement	Chemical stabilisation additive
GDL (WP5 subscale)	SGL 22BB	

3.2 Performance

The results presented in Figure 1 show the performance of the IMMORTAL SoA Baseline MEA in the JMFC 50 cm^2 screener cell. This is not indicative of the ultimate performance expected in the stack testing due to different flow-field designs and thermal envelope, but is being used as a reference for down-selection testing and to show indicative performance in sample screening.

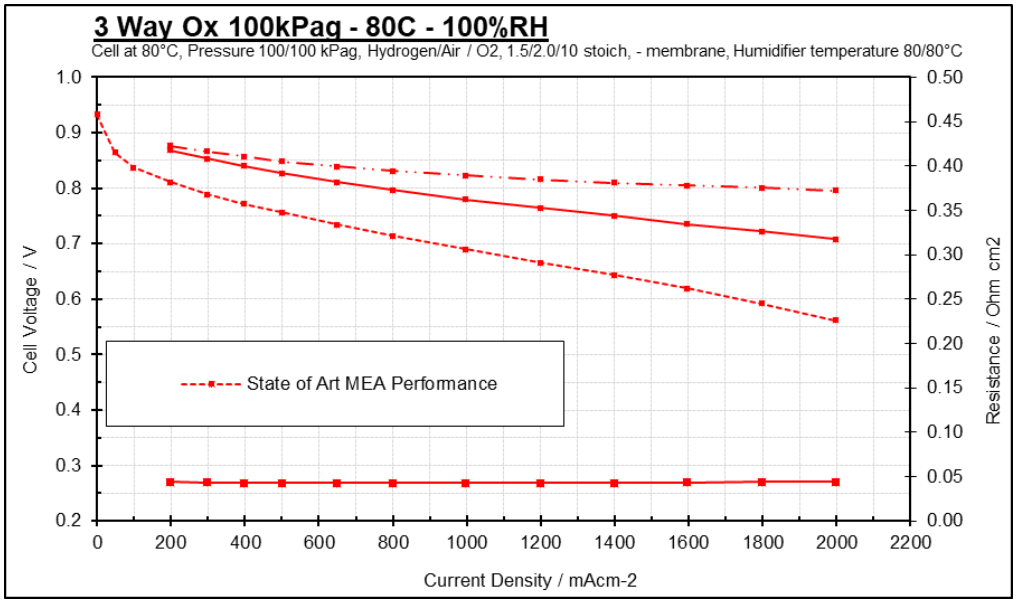

Figure 1: Performance of IMMORTAL State-of-Art Baseline MEA in JMFC screener cell for reference. Symbols (bottom to top): big squares with full line: (high frequency) resistance (HFR), small squares with dashed line: polarisation curve in air, small squares with full line: polarisation curve in oxygen, small squares with dash-dotted line: HFR-corrected polarisation curve in oxygen.

Figure 2 shows the stack performance of the IMMORTAL SoA Baseline MEA. The SoA Baseline MEA had a BOL stack performance of 0.607 V @ 1.77 A/cm^2. This falls short of the IMMORTAL performance target of 0.675 V @ 1.77 A/cm^2 by 68 mV at BOL. In comparison, the JMFC screener cell performance was 0.592 V @ 1.8 A/cm^2, which is 15 mV lower than the stack performance. This allowed WP5 to set a provisional screening exercise performance target of approximately 0.660 mV @ 1.8 A/cm^2. Through optimisation of the MEA construction, catalyst layer composition and membrane properties, it is believed that future generations of IMMORTAL MEAs will be able to achieve this performance target.

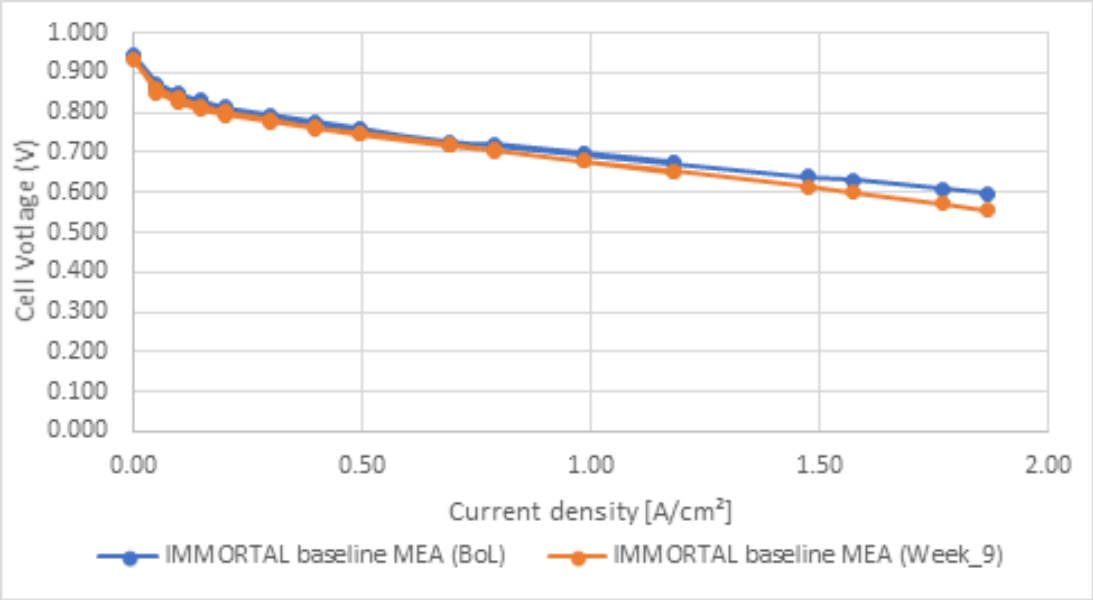

Figure 2: Performance of IMMORTAL SoA Baseline MEA in stack. H_2/air, Coolant inlet 68 °C, 2.2 bara anode inlet, 2.0 bara cathode inlet, stoichiometries 1.5/1.6 on anode/cathode, anode inlet dew point 48.2 °C, cathode inlet dew point 52.7 °C.

3.3 AST Durability

3.3.1 Pt Dissolution

Pt dissolution screening was conducted using the DOE protocol[1] under the following conditions:

- Square-wave potential cycling: 0.60-0.95 V
- Anode feed: H_2 and cathode feed: N_2
- Temperature: 80 °C

The screener cell Pt dissolution results presented in Figure 3 show that the SoA Baseline MEA had significant surface area loss, as well as significant performance loss compared to the beginning of life. Results from the stack ASTs will be compared to these results to determine if this degree of acceleration is a suitable indicator of performance loss. Comparing the SoA Baseline MEA metrics with the targets set by the DOE (Table 2) revealed that the SoA Baseline MEA did not meet the targets set for either mass activity loss or EPSA (electrode platinum surface area) loss. It will be important for future IMMORTAL MEAs to meet these targets and especially to prevent EPSA loss at even higher current densities (1.8 A/cm^2).

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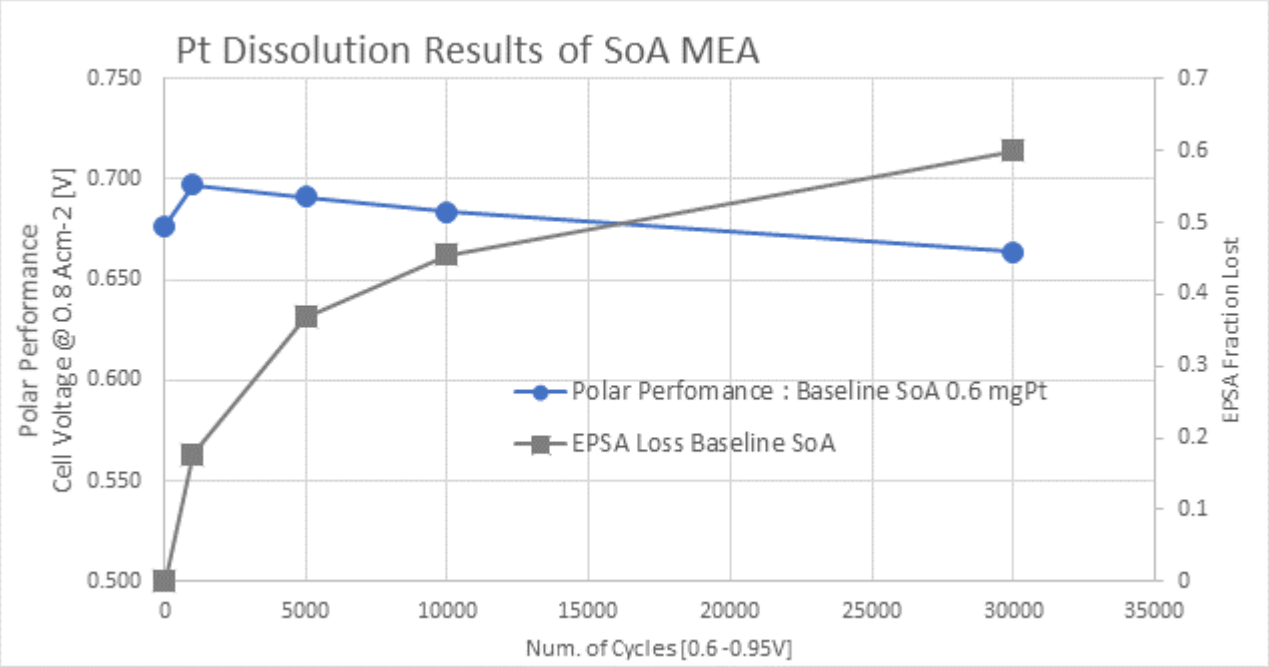

Figure 3: Results from Pt dissolution testing of IMMORTAL State-of-Art Baseline MEA.

Table 2: SoA Baseline versus DOE targets – Pt dissolution testing

Metric	SoA Baseline MEA	DOE Target
Mass Activity Loss	55.4%	<40%
Performance Loss	33 mV at 0.8 A/cm^2	<30 mV loss at 0.8 A/cm^2
EPSA Loss	59.9%	<40% loss of initial area

3.3.2 Carbon Corrosion

Carbon corrosion screening was conducted under the following conditions:

- Triangle-wave sweep: 1.0-1.5 V
- Anode feed: H_2 and cathode feed: N_2
- Temperature: 80 ^oC

The carbon corrosion results presented in Figure 4 and Table 3 show that the SoA Baseline MEA was unable to complete the full 5000 cycles of this test. Note that the performance observed at the beginning of life in this test was lower than in the Pt dissolution test due to different flow-field plates being used, as the high potentials used in the carbon corrosion testing would have damaged the plate sets used in the Pt dissolution test. It is thought that the stability of the carbon support shown here may be sufficient in a real system, as the stack can be managed to reduce or eliminate damaging air/air starts. Feedback from LPT testing will be used to understand if carbon corrosion is a key degradation mechanism that needs to be addressed.

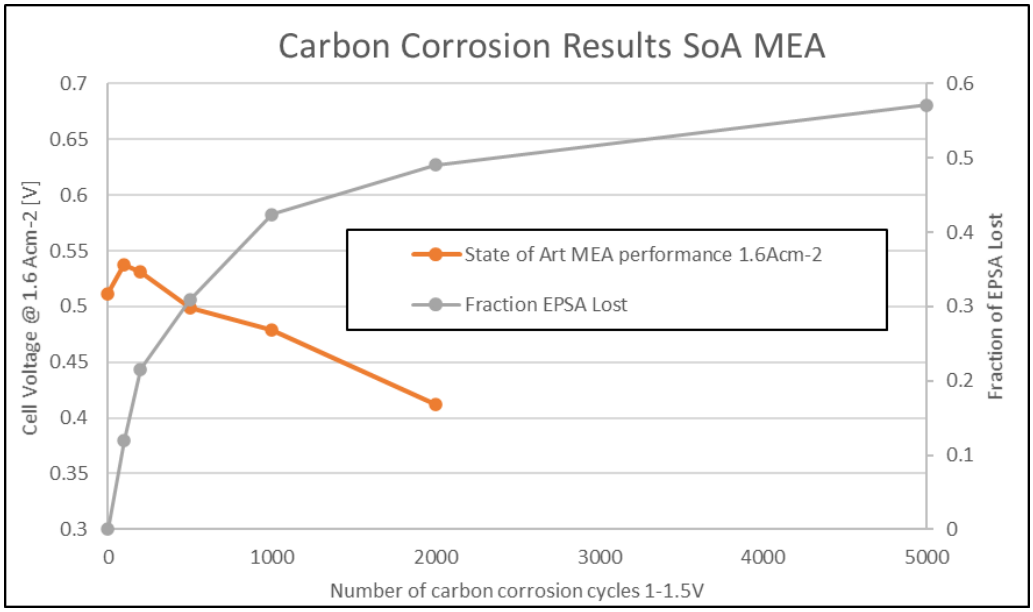

Figure 4: Results from carbon corrosion 1-1.5 V cycling of IMMORTAL SoA Baseline MEA.

Table 3: SoA Baseline versus DOE targets – carbon corrosion testing

Metric	SoA Baseline MEA	DOE Target
Mass Activity Loss	>>40%	<40%
Performance Loss	>>30 mV	<30 mV loss at 1.5 A/cm^2
EPSA Loss	57.1%	<40% loss of initial area

3.3.3 Membrane ASTs

The membrane chemical stability test for the IMMORTAL SoA Baseline MEA is shown in Figure 5; it was tested at 90 °C, 30% RH, 50 kPa and on H_2/air. The SoA Baseline MEA achieved 400 hrs in this test with the open circuit voltage (OCV) still >0.9 V (DOE Fuel Cell Technical Team Roadmap, 2017[1]). The membrane failed with excessive crossover after approximately 550 hrs.

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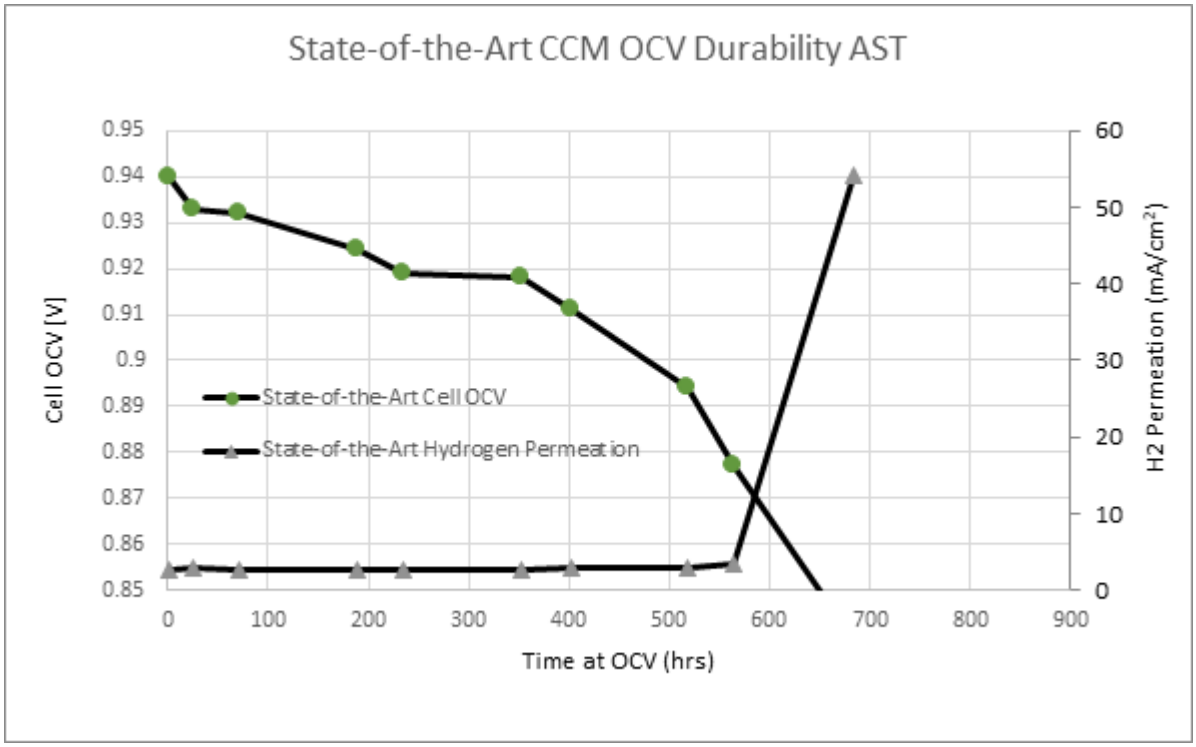

Figure 5: OCV degradation results to assess chemical stability of IMMORTAL SoA Baseline MEA membrane.

Figure 6 shows the results from the combined chemical and mechanical durability test of the SoA Baseline MEA. This test was conducted as per the DoE FCTT roadmap 2017[1]. In this case the MEA achieved >40,000 cycles before failure started to occur, indicative of crossover.

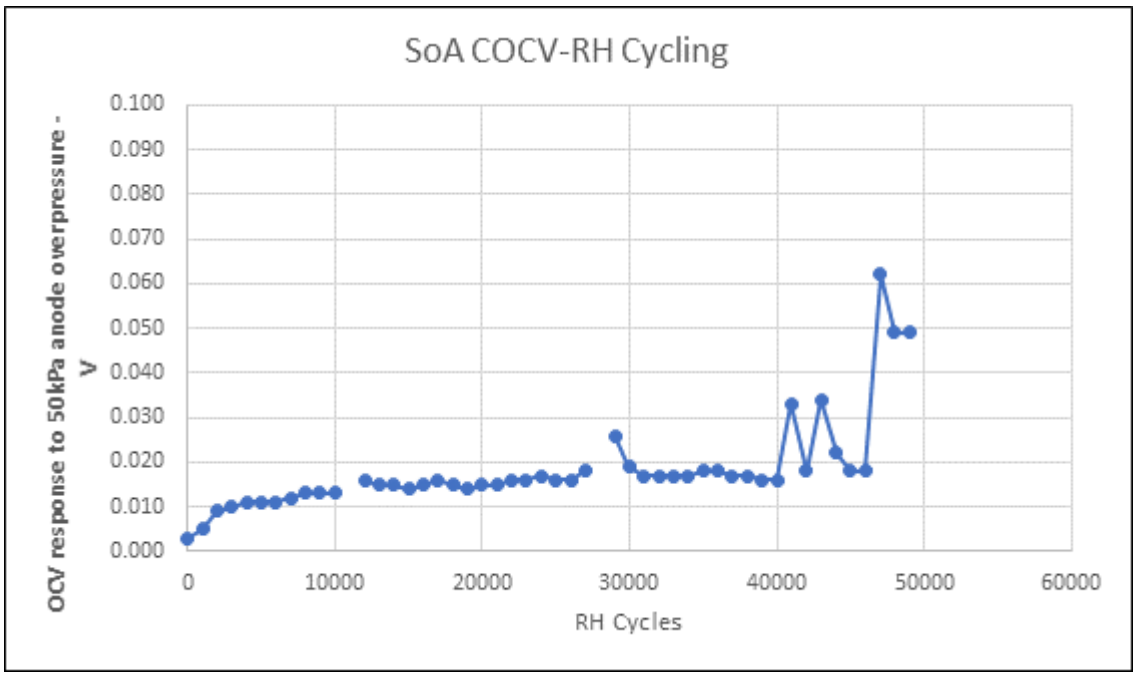

Figure 6: OCV response from combined OCV/RH cycling membrane degradation test for IMMORTAL SoA Baseline MEA.

3.4 LPT Durability

Figure 7 shows a schematic of the LPT (Load Profile Test) profile used in the IMMORTAL project for stack durability testing.

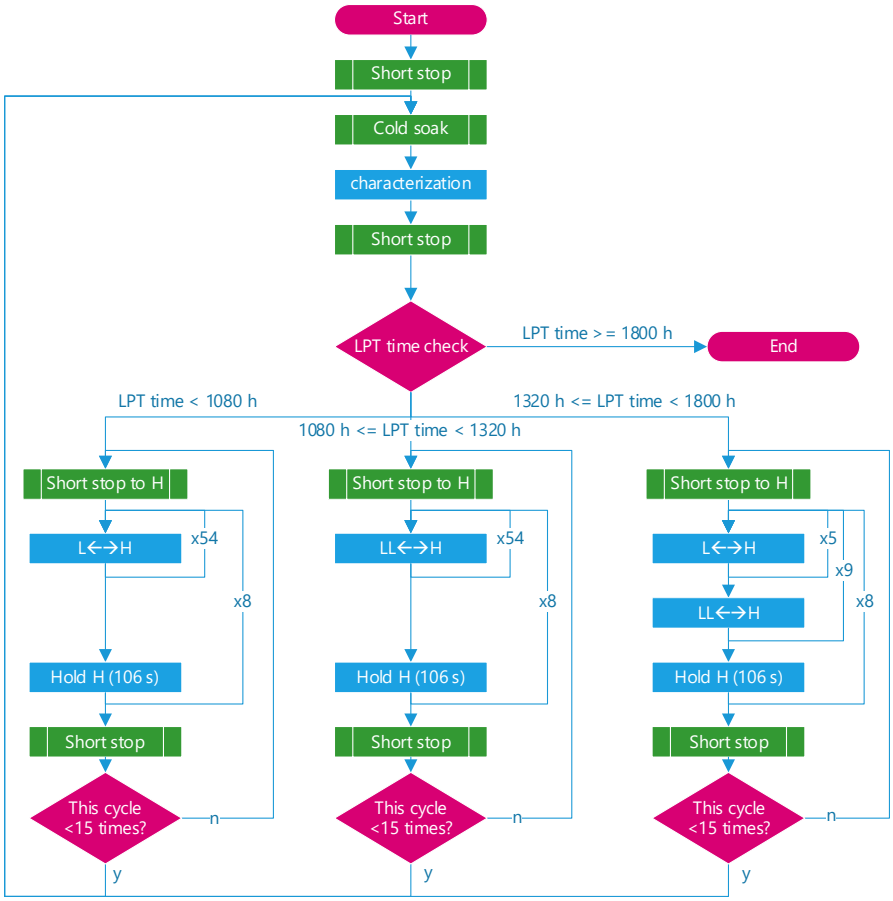

Figure 7: LPT protocol. Note that the second segment (1080 h ≤ LPT time ≤ 1320 h) was prolonged by 120 h compared to the initial experimental plan (cf. public deliverable report D2.1) and the third segment shortened by the same amount of time.

The stack LPT voltage decay rates for the IMMORTAL Baseline MEA are shown in Figure 8. Points for the first 500 hrs are not shown due to these being conducted at incorrect test conditions during the cycling portion of the test. Figure 2 shows the polarisation curves for the stack at the BoL and Week 9 characterisation steps. Comparison of the decay rates from this characterisation and LPT at similar current densities showed that the decay rate at 0.1 A/cm^2 was similar to the corresponding to LPT point L (see Figure 8); however, at 1.5 A/cm^2 the decay rate from characterisation was found to be 0.0266 mV/h compared to 0.0499 mV/h decay in the LPT. Operating conditions between these two tests were similar, the only obvious differences being a 70% anode hydrogen composition [in the LPT] versus a 100% anode hydrogen composition [during characterisation], and that the characterisation data was collected after a cold soak recovery step, indicating that some of the losses in the LPT are recoverable.

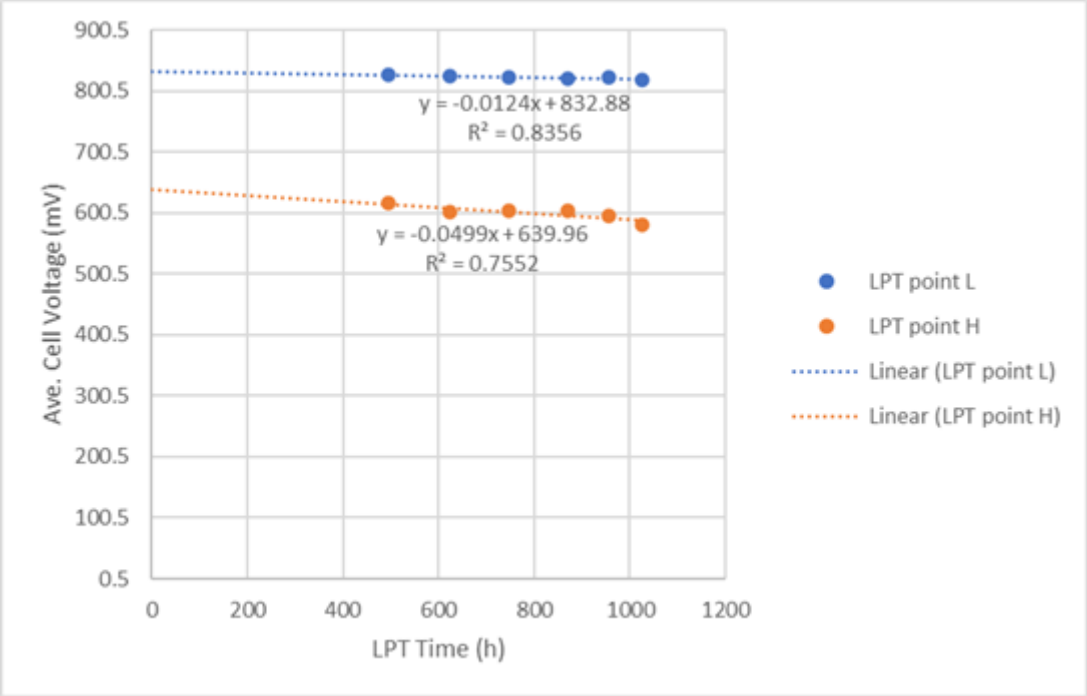

Figure 8: Stack LPT voltage decay of the SoA Baseline MEA.

3.5 Characterisation BOL/EOL

3.5.1 BOL/EOL TEM Characterisation

3.5.1.1 Sample preparation

The samples were scraped from the electrode and then ground between two glass slides and dusted onto a holey carbon-coated Cu TEM (transmission electron microscopy) grid. The samples were examined in the JEM 2800 (Scanning) Transmission Electron Microscope using the following instrumental conditions: Voltage kV 200; C2 aperture (µm) 70 and 40. Dark-field imaging was conducted in scanning mode using an off-axis annular detector. The SE signal was acquired simultaneously with other STEM images providing topological information of the sample.

3.5.1.2 TEM Characterisation

Figure 9 and Figure 10 show the IMMORTAL SoA Baseline MEA catalyst before and after Pt dissolution and carbon corrosion AST protocols respectively. From the SEI (Secondary Electron Image) images shown in Figure 9, it can be seen that there was a reduction in the density of the external Pt nanoparticles (NPs) of the carbon support, as well as an apparent increase in their average size.

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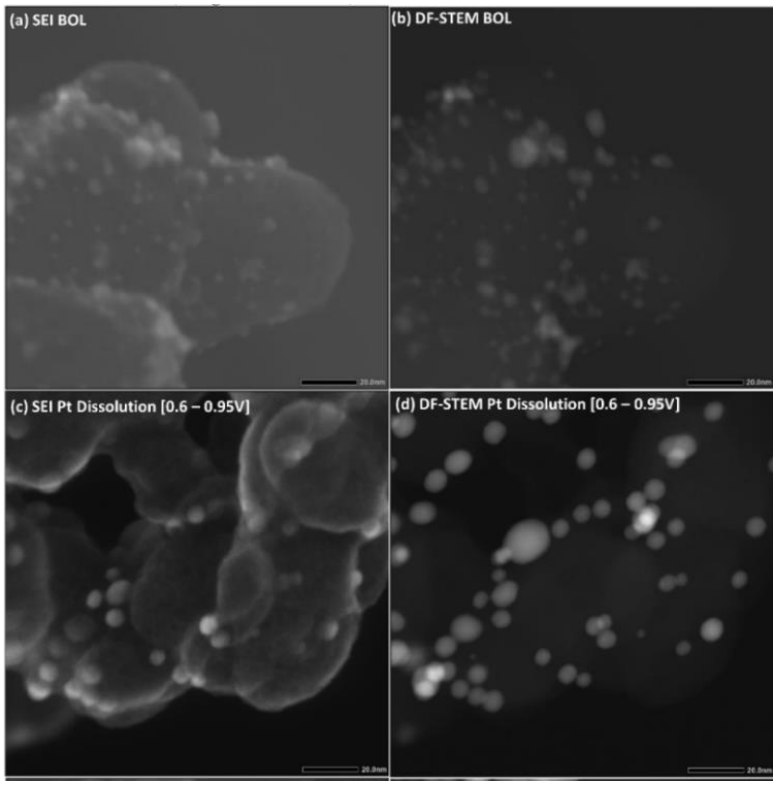

Figure 9: SEI TEM and DF STEM images of IMMORTAL Baseline MEA cathode catalyst: (a & b) BOL, and (c & d) after Pt dissolution [0.6-0.95 V].

From the SEI images shown in Figure 10, it could be seen that after carbon corrosion the number of Pt NPs on the surface of the support became greatly reduced [Figure 10 (c)] and, in some cases, none could be observed [Figure 10 (e)].

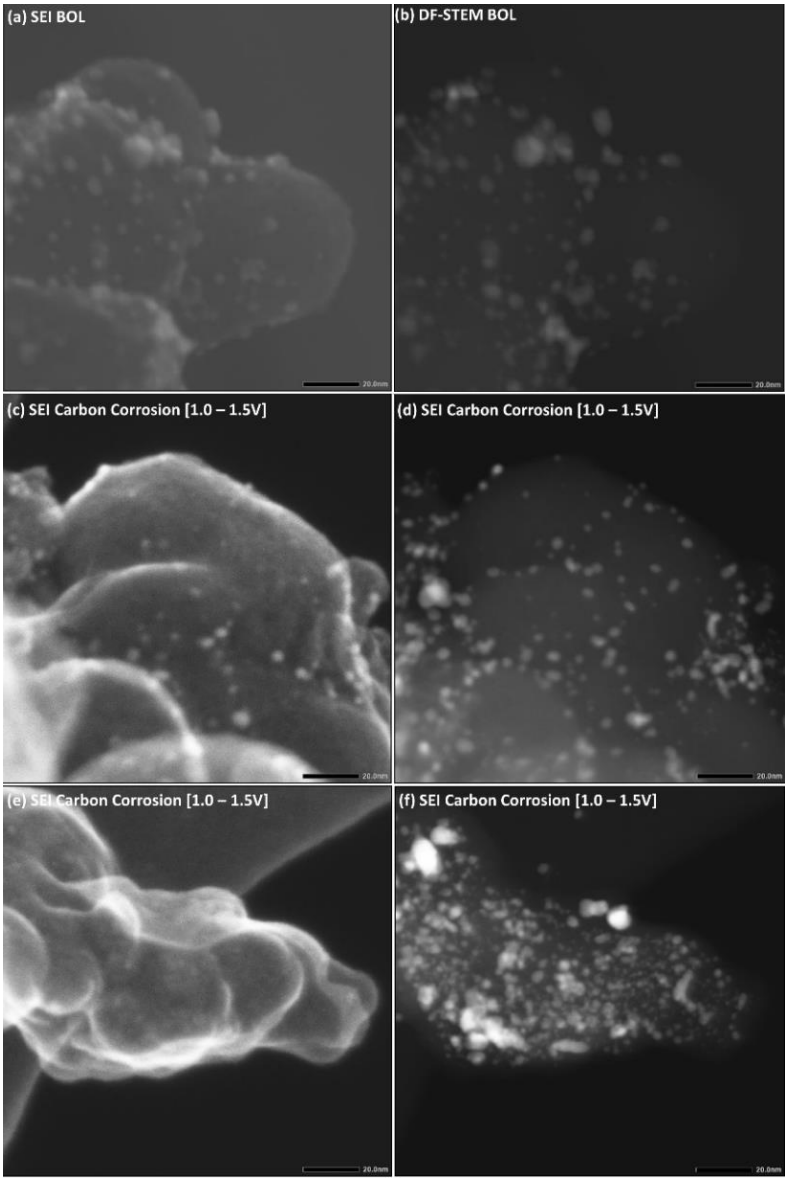

Figure 10: SEI TEM and DF STEM images of IMMORTAL Baseline MEA cathode catalyst: (a & b) BOL, and (c ,d, e & f) after carbon corrosion [1.0–1.5 V].

3.5.2 SEM Characterisation

SEM (scanning electron microscope) images of the IMMORTAL SOA Baseline MEA after Pt dissolution shown in Figure 11 revealed a Pt dissolution band (a band of Pt formed in the membrane) in both cases (b) and (c). The ability to compare these dissolution bands in detail via SEM analysis was not possible due to insufficient image resolution. No thinning of the anode, cathode or membrane was observed. Furthermore, no sign of membrane degradation was observed.

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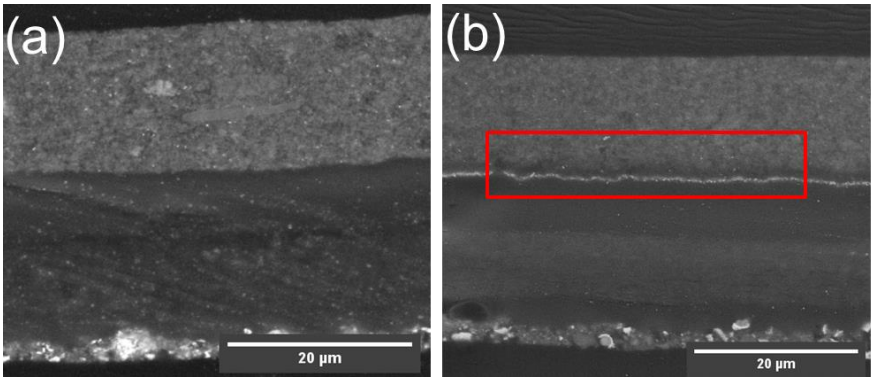

Figure 11: SEM images of IMMORTAL Baseline MEA: (a) BOL, and (b) after Pt dissolution [0.6-0.95 V].

3.6 SEM of Returned LPT Parts

After the load profile stack testing, the IMMORTAL SoA Baseline MEAs were returned to JMFC and analysed by SEM. Figure 12 shows a collage of images of the SoA Baseline MEA. The top left image is the CCM (catalyst coated membrane) at beginning of life. The other images labelled as LPT A, B and C were taken from the active area at anode inlet, centre of the MEA and cathode inlet respectively. What can clearly be seen in all the tested images is a membrane deformation where the membrane has conformed to the GDL (gas diffusion layer) under load. Also of note is that there was no sign of a platinum dissolution band in the membrane of the LPT MEAs after testing.

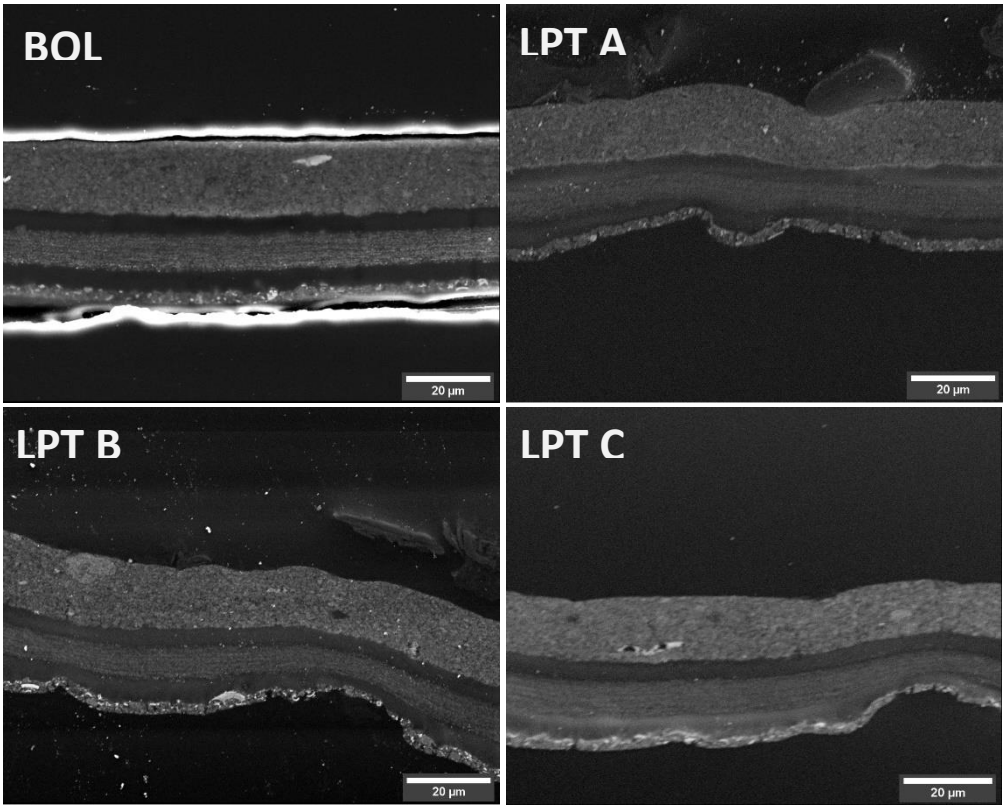

Figure 12: SEM cross-sections of beginning of life CCM, LPT A anode inlet, LPT B centre of MEA and LPT C cathode inlet regions.

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Thickness measurements of the membrane are shown in Figure 13. The SoA baseline MEA had a membrane thickness of approximately 18 µm, but as this was a tested MEA it is possible that there had been some swelling of the membrane as a result of operation. The average membrane thickness was slightly reduced in each case for all of the tested regions. The centre of the MEA appeared to be the least thinned, with both inlets showing a slightly reduced membrane thickness.

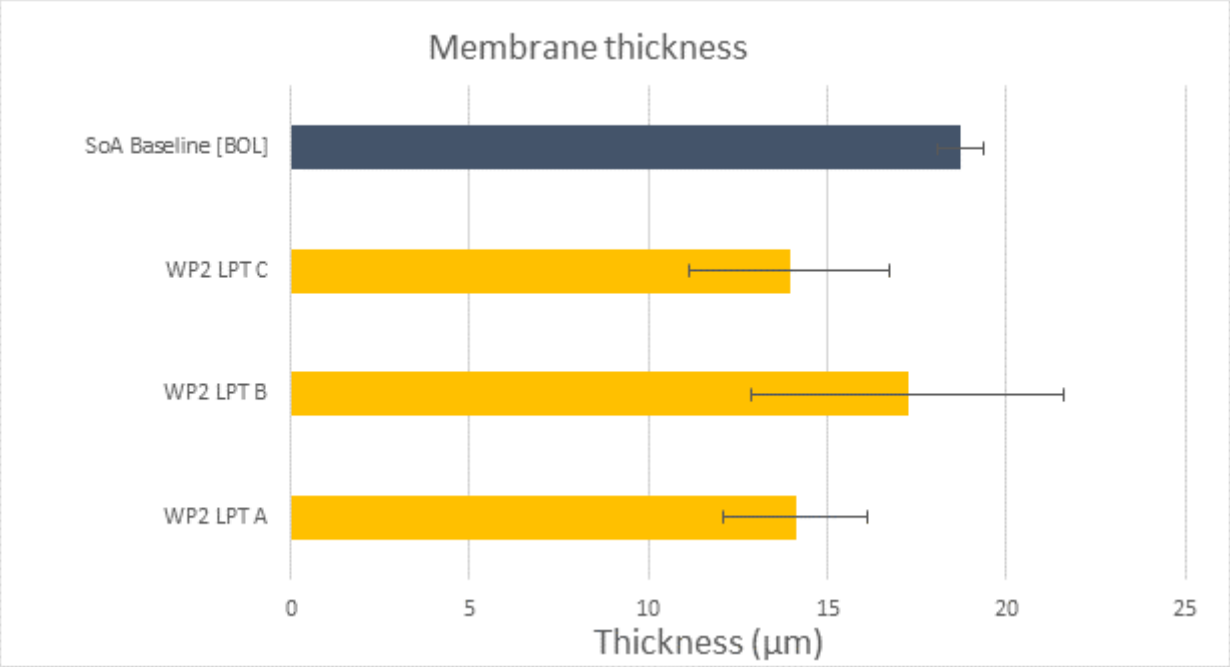

Figure 13: Average membrane thickness measured from the SEM images

Figure 14 shows the TEM images of the cathode catalyst layer at three positions along the MEA. It can be seen by comparing these images to those in Figure 10 that no significant carbon corrosion had occurred, as there were still significant quantities of Pt NPs on the carbon surface. Although there was no Pt dissolution band visible in the membrane of the LPT MEAs, it is likely that the surface area loss is primarily due to agglomeration or dissolution of the Pt NPs during the LPT. This will be investigated in future work in WP5.

TEM analysis also showed that the growth of the Pt particles appeared to occur differently in the stack LPT compared to the ASTs, with the LPT showing more growth of particles within the carbon support than seen after applying the ASTs. It was therefore concluded that the AST could not fully predict LPT degradation.

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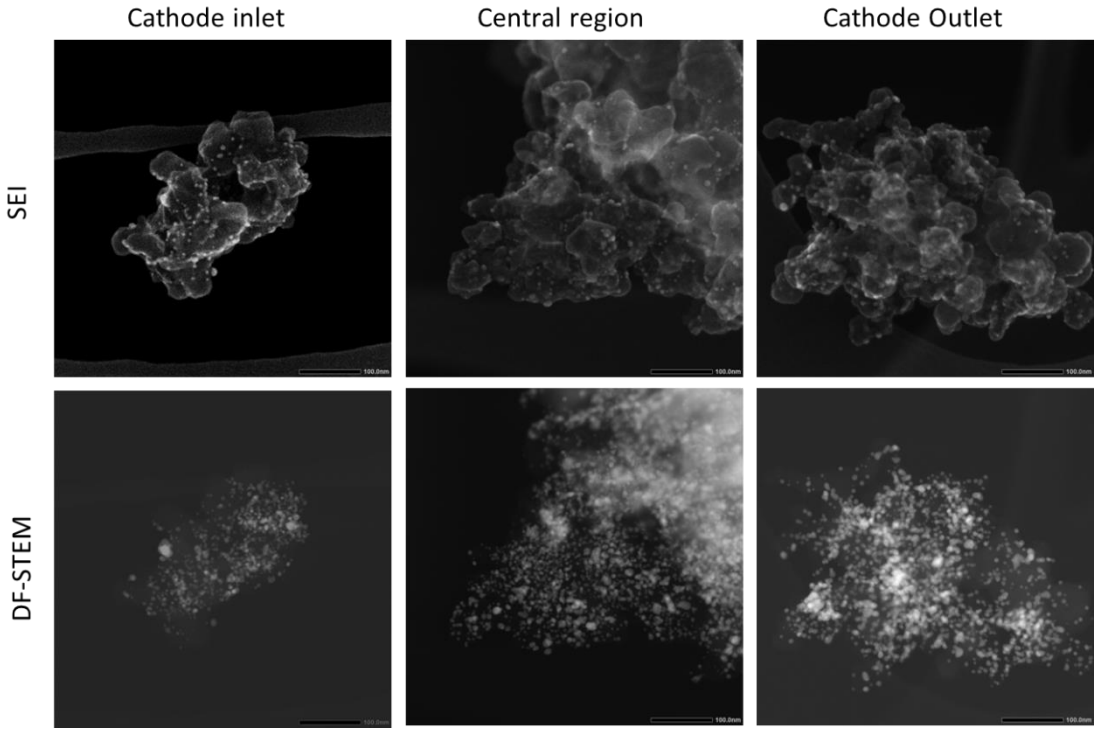

Figure 14. SEI and DF-STEM Images of cathode catalyst sampled from the cathode inlet, central region and cathode outlet of the IMMORTAL Baseline MEA post LPT protocol.

4 Conclusions and Future Work

In conclusion, the SoA Baseline MEA provided as a benchmark for the IMMORTAL project did not meet the project requirements for a HD specific MEA. All aspects of the performance of the MEA need to be improved to be able to meet the project targets.

The MEA performance was below target, and will require optimisation of the catalyst, layer composition, membrane properties and MEA construction, to meet the stated targets.

The MEA did not pass all of the DoE AST tests and, in stack level load profile testing, decay rates of up to 50 µV/hr were observed.

Post-mortem testing of the tested stack parts showed some membrane thinning, but no clear signs of Pt dissolution in the membrane. Some catalyst layer thinning was observed that may be consistent with some carbon corrosion.

TEM analysis of the stack LPT samples showed Pt particle growth, but with an apparent difference between how primary particles behaved compared to the AST. It was therefore concluded that the AST could not fully predict LPT degradation.

Future work in IMMORTAL will focus on optimisation of the MEA for HD operation.

5 References

1. 2017. DOE *Fuel Cell Technical Team Roadmap*. U.S. Department of Energy, pp.22-23.