ID-FAST - Investigations on degradation mechanisms and Definition of protocols for PEM Fuel cells Accelerated Stress Testing

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D4.1: Definition of new reference single cell hardware (M8)

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Summary

The deliverable report D4.1 describes the actions and results regarding the selection of a differential test cell hardware, which will be used within the project ID-FAST. Two single test hardwares are considered: the one developed by JRC which was identified as the nominal case in the description of the project, as it is planned to be an harmonized european cell, and the one jointly developed by Fraunhofer ISE and the German SME baltic Fuel Cells GmbH, which was available earlier. Both are differential cells (so-called "zero gradient cells" in the description of work) allowing homogeneous operating conditions along the surface, in order to analyse properly the impact of stressors for the development of accelerated stress test protocols.

More tests will be conducted with the harmonized JRC cell in the future and described in other reports of the ID-FAST project.

Revisions

Version	Date	Author(s)	Commments *(inputs added, revision, approval…)*
1	17.07.2019	U. Groos (Fraunhofer ISE)	First draft
2	29.07.2019	A. Casalegno (Polimi)	Improvement and inputs
3	08.08.2019	U. Groos (Fraunhofer ISE)	Additional inputs with tests in selected conditions
Final	28.08.2019	S. Escribano (coord., CEA)	Last version revised improved for submission

Contents

List of Abbreviations

AST	Accellerated Stress Test
BOL	Begin of Life
BOT	Begin of Test
CCM	Catalyst Coated Membrane
CL	Catalyst Layer
CV	Cyclic Voltammetry
DP	Dew Point
DPT	Dew Point Temperature
ECSA	Electrochemically active Surface Area
EIS	Electrochemical Impedance Spectroscopy
EOL	End of Life
EOT	End of Test
GDL	Gas Diffusion Layer
JRC	Joint Research Center of the European Commission
MEA	Membrane Electrode Assembly
NDA	Non Disclosure Agreement
NEDC	New European Driving Cycle
RH	Relative Humidity

List of symbols

F	Faraday constant
$\lambda_{fuel/ox}$	Fuel (anode) / oxidant (cathode) stoichiometry
T	Temperature
$p_{abs/g}$	Absolute / Gauge (i.e. over-) pressure
Δ	Difference

1. Introduction

The ID-FAST project deals with the development of accelerated stress test (AST) protocols for PEMFC in automotive applications. Going beyond the usual approach, the AST protocols shall be connected with realistic ageing as in vehicle operation by means of quantification. This requires the deduction of transfer functions from “real world operation” to AST operation and vice versa.

As a basis for the development of the AST protocols all material testing results should be realized by the same test hardware and testing procedures. Therefore a reference single cell test hardware had to be defined.

A task is dedicated to the definition of a reference single cell test hardware to be adopted for AST testing. New single cell design studied by the working group coordinated by JRC with the aim to contribute defining an international standard, was particularly considered in this task. The work was also conducted in collaboration with the members of the international Advisory Group (Fraunhofer ISE was a member) involved in harmonisation and standardisation activities worldwide, and included a statement about different single cells currently used in research activities on ASTs.

The selected hardware had to be designed and validated to ensure the highest standards in measurements and reproducibility among partners. The designed single cell test hardware, coupled with suitable operating conditions, should permit to minimise both operation and degradation heterogeneity induced by state of the art flow fields, especially regarding distribution of temperature, oxygen and hydrogen concentration and liquid water.

2. Requirements for Single Cell Test Hardware

Catalyst Layer (CL), Membrane, Catalyst Coated Membrane (CCM), Gas Diffusion Layer (GDL), and Membrane Electrode Assembly (MEA) testing has to be performed in so-called differential or zero-gradient test cells, which means that there are minimized and negligible gradients regarding gas concentration, humidity, and temperature. These very well defined operation conditions are needed to evaluate material properties only without any interdependence of e.g. flowfield designs. The main research question behind this is “what are the (material) properties of a certain component?” and the intention is to evaluate cell components in order to analyse losses due to material aspects. In contrast to that a stack developer might be interested in the design question “what component suits best to my specific cell design and my specific operation strategy?”, so in stack development one is interested especially in the dependencies of the MEA to cell design.

As with state-of-the-art CCMs and MEAs very high current densities up to 5 A/cm² (at potentials below 400 mV) are realized, an efficient cooling of the test cell hardware is crucial to keep differential conditions. Usually this leads to liquid cooling concepts along with the need of an additional cryostat. Flowfield design has to minimize channel-land effects and typically very narrow channel-land designs and parallel channels are proposed. Regarding the active area a good compromise of negligible edge effects and homogenous operating conditions over the active area has to be realized. This leads to typical active areas of 5 to 25 cm² and the need for laminating frames on the CCM to realize a well defined active area. Compression has to be well defined over the whole active cell area with the need for either very rigid compression plates with a number of screws or pneumatic compression sets. All sensors must be placed as near as possible to the point of interest to assure high quality sensor signals. The test cell hardware has to use highly corrosion resistant material especially if long-term testing or degradation analysis is intended.

Regarding measurement effort an easy handling of the hardware is appreciated. Also availability of the hardware should be considered.

Within this report hardware cost issues are not discussed.

3. Investigated Single Cell Test Hardware

At project start some advanced test hardwares were already used by industry but unfortunately they were only available under the obligation of signing non disclosure agreements. This means that results with the industry test cells could only be published with written permission from the test cell hardware provider. As this is not suitable for officially funded projects like ID-FAST the project consortium decided to concentrate its evaluation on a test cell hardware which was under development by JRC and another test cell hardware which was developed by Fraunhofer ISE and is already commercialiced by the German SME Baltic Fuel Cells GmbH (without NDA obligation).

3.1 JRC Test Cell Hardware

Unfortunately the consortium did not have the chance by now to perform own tests with this hardware as development and manufacturing was not finished until July 2019. Also, the project partners had to sign a NDA with JRC prior of ordering the hardware.

The flowfield and channel-land design was discussed intensively within the international advisory group. JRC followed the recommendation of AFCC regarding channel-land design. Pressure drop within the active area was designed to be below 3 kPa for cathode and anode with stoichiometries of 10 / 8 and current densities of 4 A cm^{-2}. A crucial design rule was to assure laminar flow and even gas velocities within the active area, thus JRC decided for a larger inlet area.

The active area is 50 x 20 mm^2, so 10 cm^2 in total. The channel cross section is 0.25 x 0.25 mm^2, pitch 0.84 mm for anode and 0.6 x 0.4 mm^2, pitch 0.84 mm for cathode. Graphitic plates are used as flow field plates.

Temperature control of the test cell is an important issue, therefore JRC decided to implement 10 thermocouples along the gas flow direction – 5 for cathode and anode. The sensors are about 3 mm away from the MEA. Liquid cooling is realized in the back side of the flow field plate. According to JRC test results the temperature gradient within the active area is below 1.5 K even at current densities up to 5 A cm^{-2}.

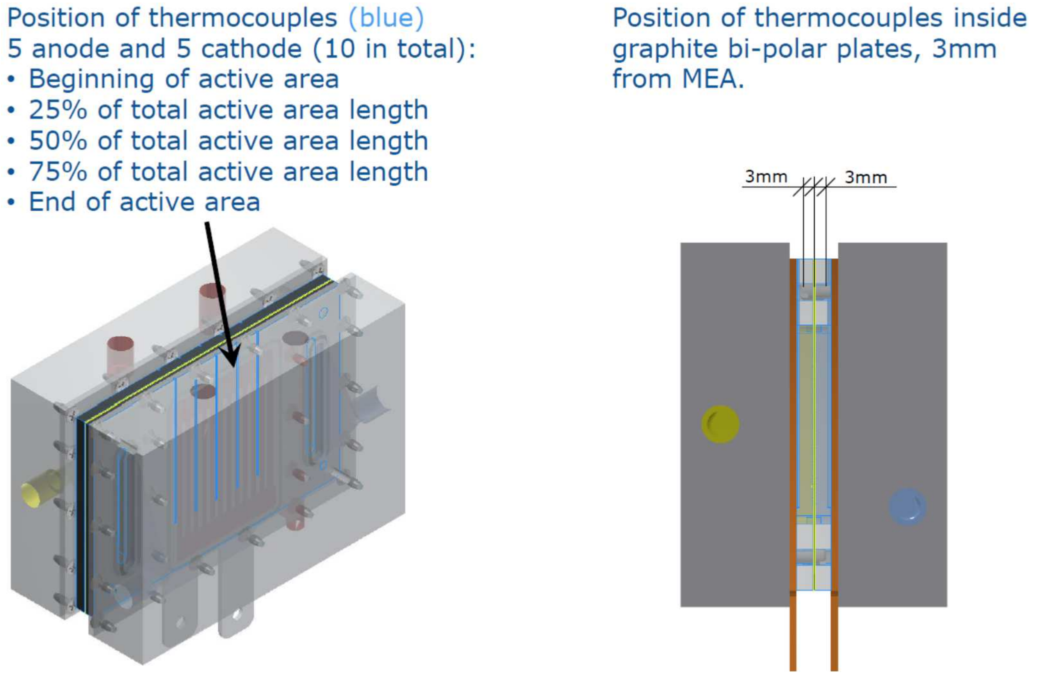


Figure 1: Temperature control of JRC test cell hardware

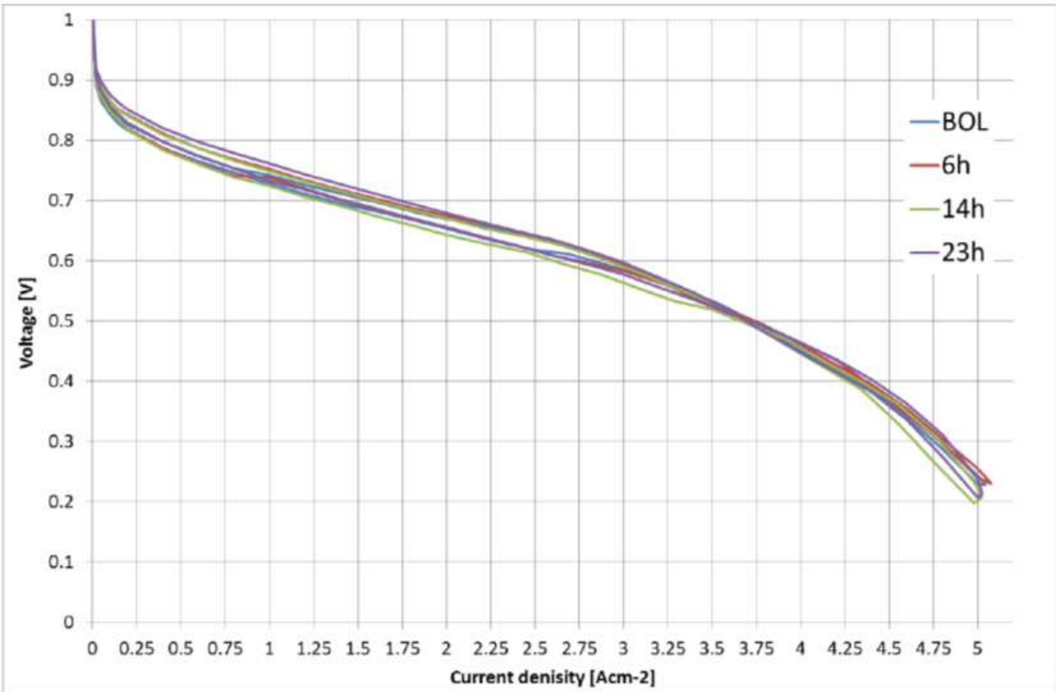


Figure 2: Reproducibility of JRC test cell: Test results of JRC with one MEA.

3.2 Baltic Test Cell Hardware

Baltic has licensed a test cell hardware design from Fraunhofer ISE, which is based on the Baltic compression set. The hardware is commercialized by Baltic and can be ordered without NDA obligation.

A major design rule was to separate compression set from the cell unit, so that exchange of MEA samples is quick and easy and does not affect the media connectors of the compression set. For compression a pneumatic cylinder is used.

Figure 3: Test cell by baltic (compression set in the back, cell unit in the front)

Design guidelines of the baltic test cell were:

- easy handling by separating of cell- and compression unit
    - connection of all media by closing of pneumatic cylinder (no media connection to cell unit – exchange of test samples without (dis-)assembling pipes)
    - no coolant liquid inside cell unit (easy opening of cell unit and CCM exchange as leakage is prevented)
- Compression force exclusively on active area and not on sealings (no gaskets on CCM but radial gasket on compression cylinder)

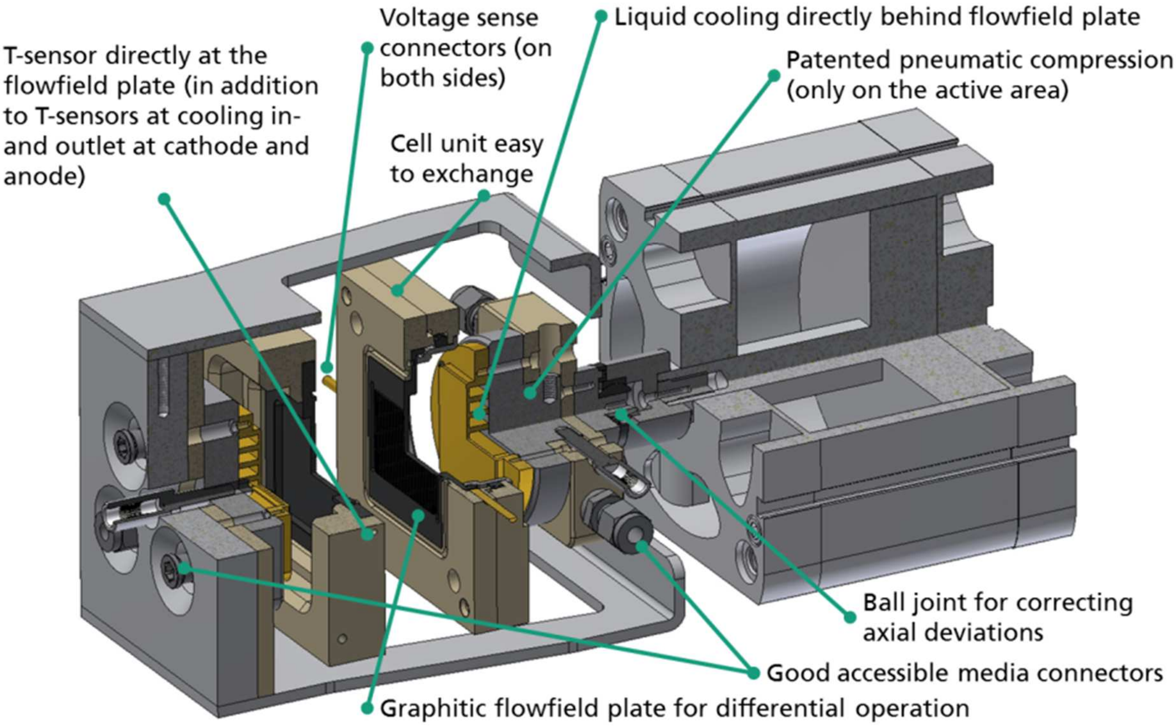


Figure 4: Design of Baltic test cell hardware

The clamping pressure is adjusted by a pneumatic cylinder, so that the cell compression is independent from GDL thickness. A ball joint leads to homogeneous compression.

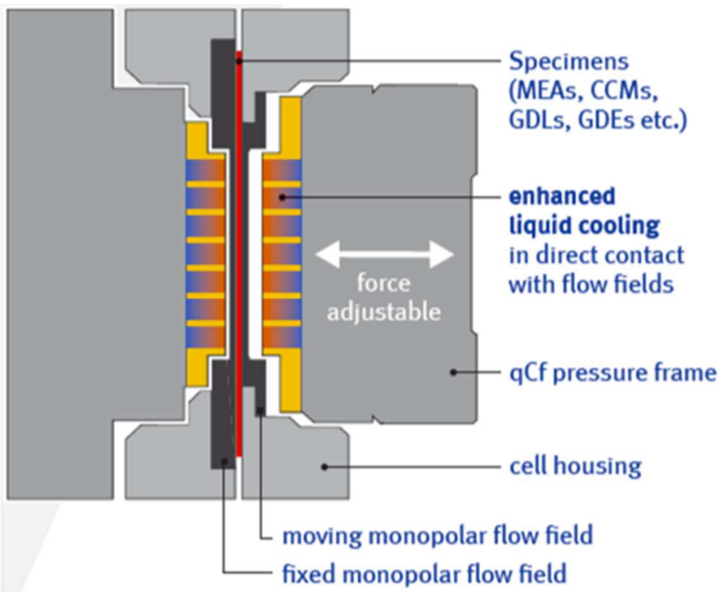


Figure 5: Design of Baltic cell unit

The active area of 30 x 40 mm² is defined by PEN frame laminated on top of the CCM. To reduce boundary effects the GDL is overlapping the CCM area.

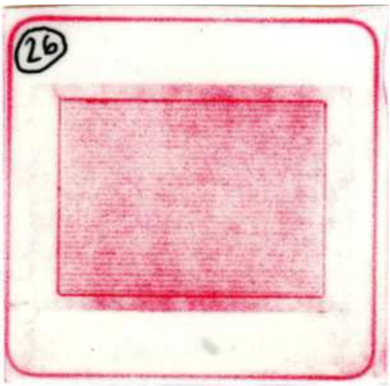


Figure 6: Even compression of the active cell area tested with pressure paper

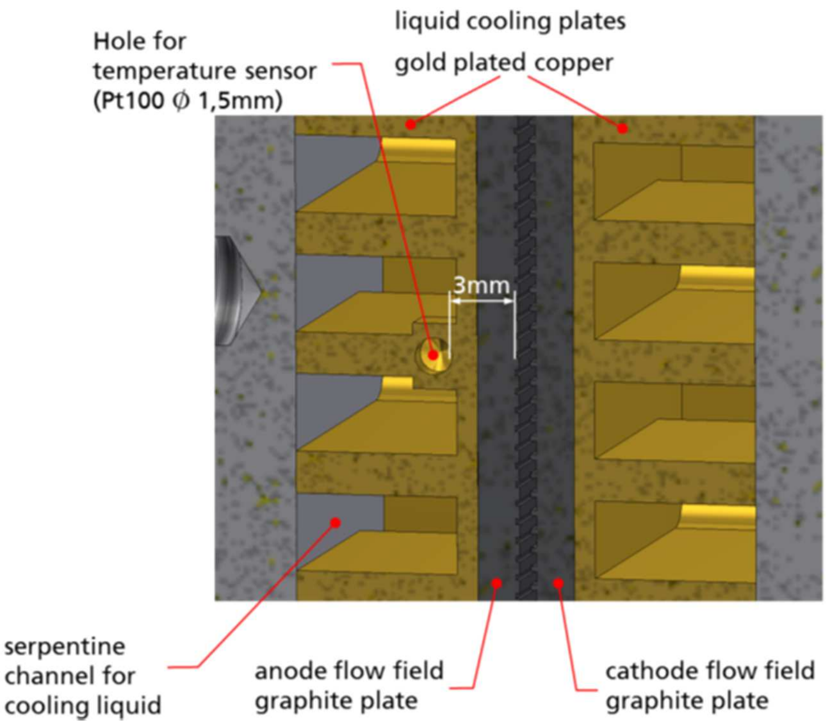


Figure 7: Liquid cooling of Baltic cell unit

The temperature sensor is placed in the cooling flowfield ca. 3 mm away from the MEA. Liquid cooling is applied. Copper parts are used for good heat conduction, but to avoid corrosion issues, these parts are gold coated. Measurements of Fraunhofer ISE showed a temperature gradient from gas inlet to outlet of well below 1 K for current densities up to 4.5 A cm-².

The flowfield design follows recommendations of AFCC and JRC. A graphitic flowfield is used.

		Cath.	An.
active cell area	cm²	12	
channel lenght	mm	45	
inflow and outflow	mm	2,5	
flowfield width	mm	30	
landing pitch	mm	0,84	
land width	mm	0,25	0,59
channel width	mm	0,60	0,24
channel depth	mm	0,25	0,17
pressure drop 5/2 nl/min, 1 bara, 100% RH	mbar	90	120
GDL size	mm	50 x 35	

Figure 8: Baltic flowfield design

Experiments of Fraunhofer ISE showed a very good reproducibility of results for the polarization curve up to current densities of 4.5 A cm^{-2}.

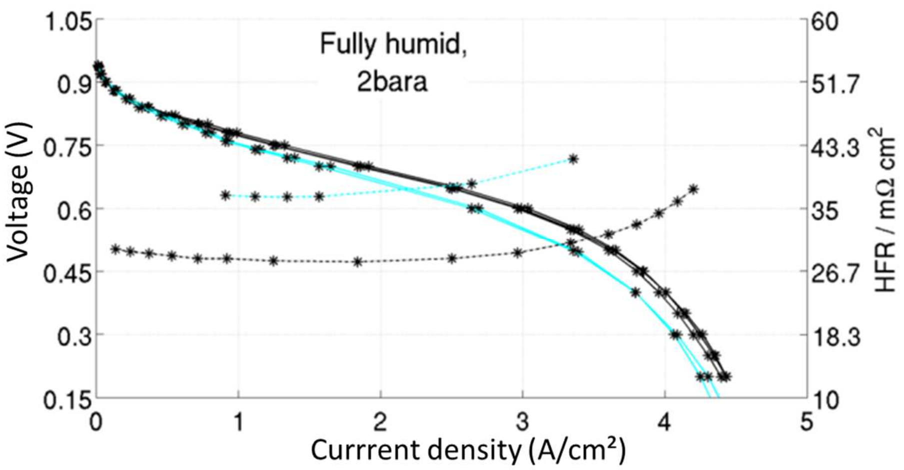


Figure 9: Reproducibility with baltic test cell hardware by using 1 MEA for several tests. Measurements of Fraunhofer ISE

4. Experimental validation of JRC and Baltic test cell hardwares

For the reference tests a CCM from JMFC type A with 0.05 mgPtcm-2 on anode and 0.4 mgPtcm-2 on cathode was used together with a Freudenberg H14CX483 GDL. The cell was operated at a constant stoichiometry of 8/10 (cathode/anode) down to a minimum current density of 0.5 A/cm².

4.1 Break-in

The break-in procedure serves to bring a virgin fuel cell or stack to full performance. The general break-in procedure as defined by the STACK-TEST project is shown below and can be found in the STACK-TEST master document (TM P-00). This procedure is defined as standard procedure witin ID-FAST, if no cell- or stack-specific procedure is available.

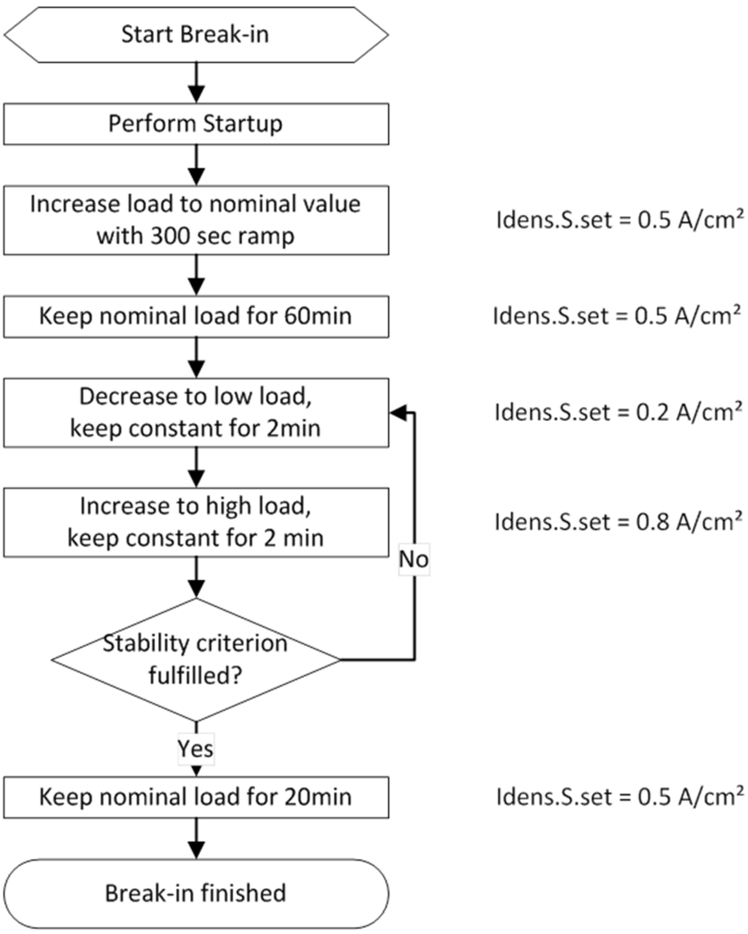


Figure 10: General break-in procedure as defined by the STACK-TEST project, figure reproduced from the STACK-TEST master document (http://stacktest.zsw-bw.de)

4.2 Test Protocol

For the accelerated stress testing (AST) the protocols from Department of Energy in US are used – the catalyst AST and the catalyst support AST (Fuel Cell Technology Office Multi-Year Research Development and Demonstration Plan 2016[1], Table P.1 'Electrocatalyst Cycle and Metrics' and Table P.2 'Catalyst Support Cycle and Metrics').

In the ID-FAST project, a driving cycle has been defined, divided into two main parts: the COLD part (at low/middle load) and the HOT part (at middle/high load). Since the local operating conditions in a full-scale cell mainly depend on the specific configuration of the flow-fields that is adopted in the stack, some assumptions have been done, in order to propose a set of polarization curves, representative as much as possible of State of Art system, without facilitate a specific solution. In particular counter-flow configuration was chosen (as the most adopted in real system), and cooling flow was considered in the same direction of cathode feeding.

To take into account the heterogeneities that typically occurs in a full-scale cell, it was agreed to consider two sets of operating conditions, the purpose of which is to represent the INLET and the OUTLET zones, since they are considered from aged data available from previous project as the most stressed during operation. Cathode outlet operating conditions depend in general on the specific hardware adopted, and are not predictable *a priori*. So, they were obtained applying mass balances on every single point of the driving cycles.

Conditions selected this way are detailed in the Table 1.

For the data presented here, at BoT and EoT, all the polarization curves of Table 1 are performed. The polarization curves CatInCOLD (ID-FAST reference condition) and EUHarm are performed at every stop:

- Electrocatalyst AST stops: 1k / 5k / 10k / 30k
- Support AST stops: 10 / 100 / 200 / 500 / 1k / 2k

For performing the polarization curves an initial load of 0.5 A/cm² is applied for 300 s. The dwell time for each point is 180 s, whereas analysis time is 120 s. Electrochemical impedance spectroscopy is performed at: 0.4 / 1 / 1.5 / 2.0 / 3.0 A/cm² (only high to low).

[1] https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_myrdd_fuel_cells.pdf

Table 1: Variation of operating conditions for polarization curves

Code	T.Si.CL / °C	DPT.Si.C / °C	DPT.Si.A / °C	RH.Si.C / %	RH.Si.A / %	p.Si.C / kPa_{abs}	p.Si.A / kPa_{abs}	Conc.Si.C.O_2 / %	Conc.Si.A.H_2 / %
CatInCOLD	68	43	58	30	63.5	280	300	20.9	100
Oxygen	68	68	68	100	100	280	300	100	100
CatOutCOLD	68	68	53	100	50	140	190	20.9	100
EUHarm	80	80	80	100	100	230	250	20.9	100
CatInHOT	85	57	85	30	100	280	300	20.9	100
CatOutHOT	95	88	72	77	40	280	300	20.9	100

Table 2: Procedure for the polarization curve:

Sequence Low to High

Current Density	0.005	0.01	0.02	0.04	0.06	0.1	0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.5	1.6	1.8	2	2.2	2.4	2.6	2.8	3
Dwell Time /s	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180

Sequence High to Low

Current Density	3	2.8	2.6	2.4	2.2	2	1.8	1.6	1.5	1.4	1.2	1	0.8	0.6	0.4	0.2	0.1	0.08	0.1	0.04	0.02	0.01	0.005
Dwell Time /s	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180

4.3 Experimental results of Fraunhofer ISE with the Baltic test cell hardware

Fraunhofer ISE performed tests with the Baltic test cell hardware in July and August 2019 according to the protocols and materials, which are presented in chapter 6.1 and 6.2. The results are presented here.

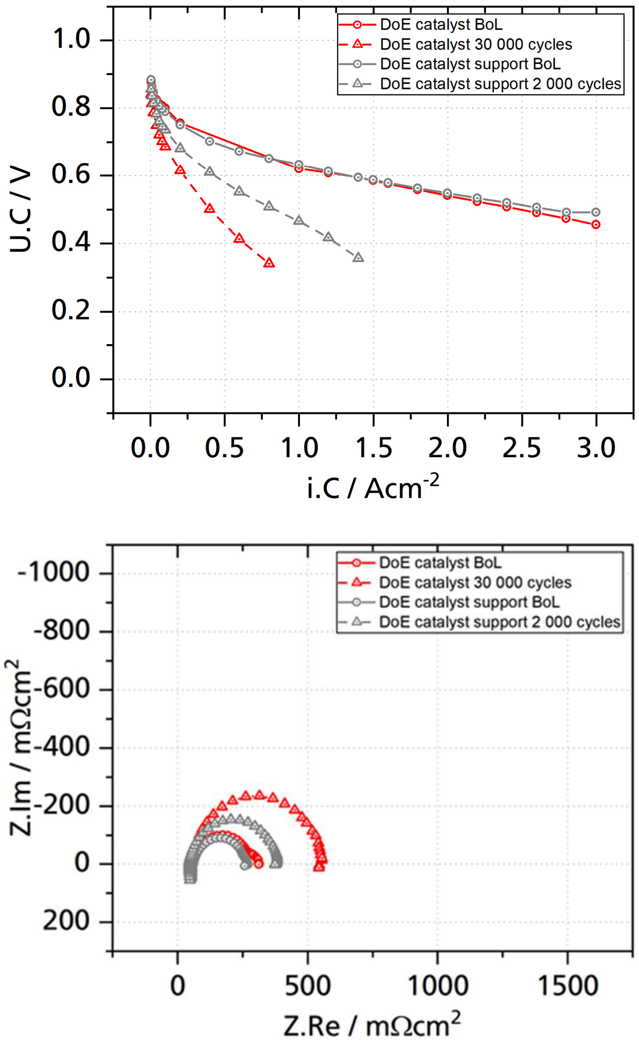
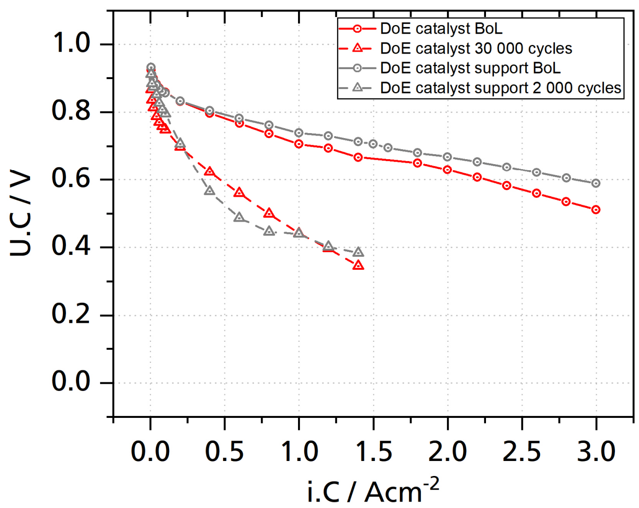


Figure 11: Polarization curve and EIS in conditions CatInCold.



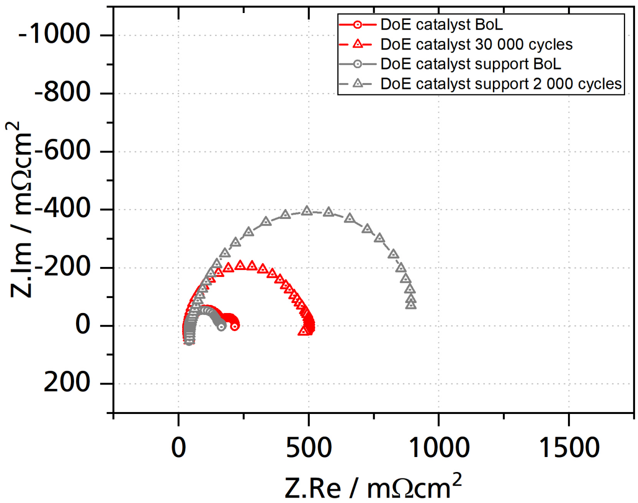
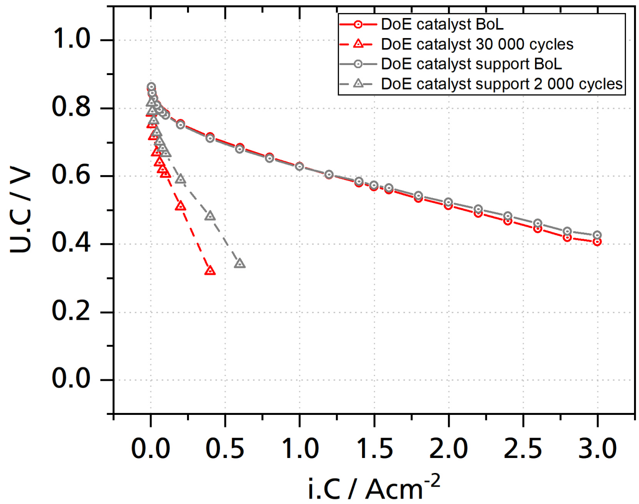


Figure 12: Polarization curve and EIS in conditions withpure oxygen.



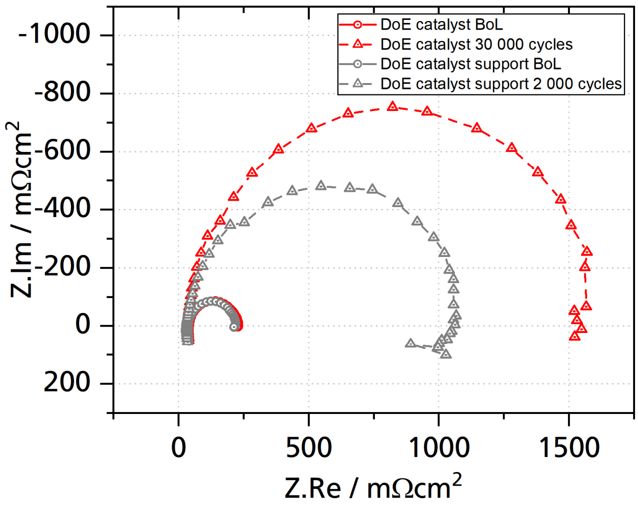
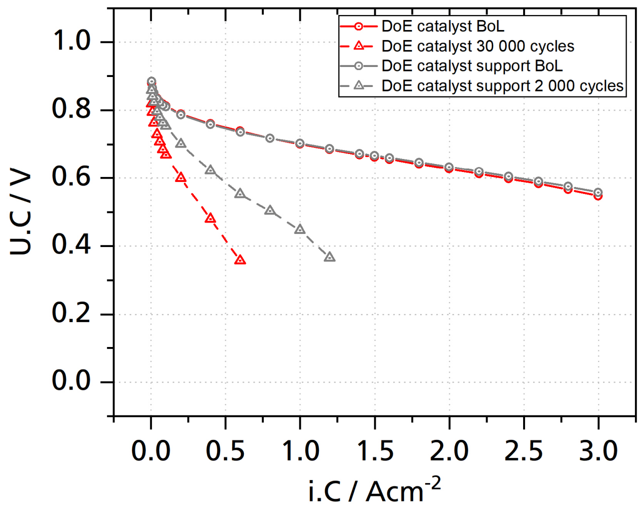


Figure 13: Polarization curve and EIS in conditions CatOutCold.



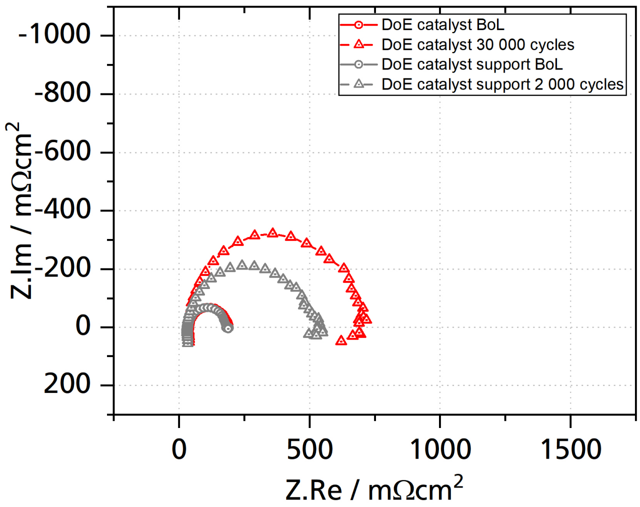
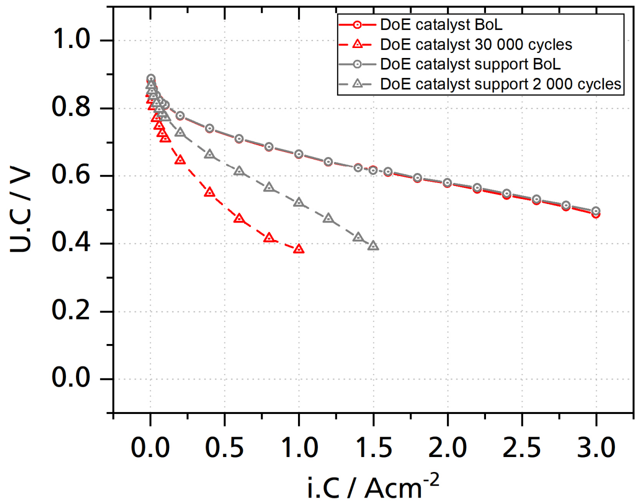


Figure 14: Polarization curve and EIS in EU harmonized conditions.



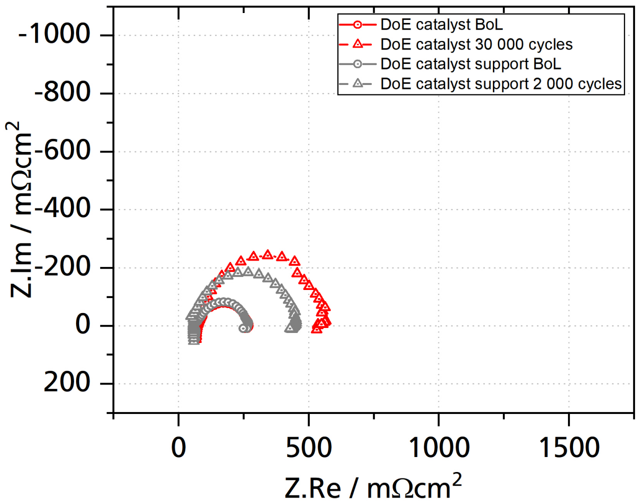
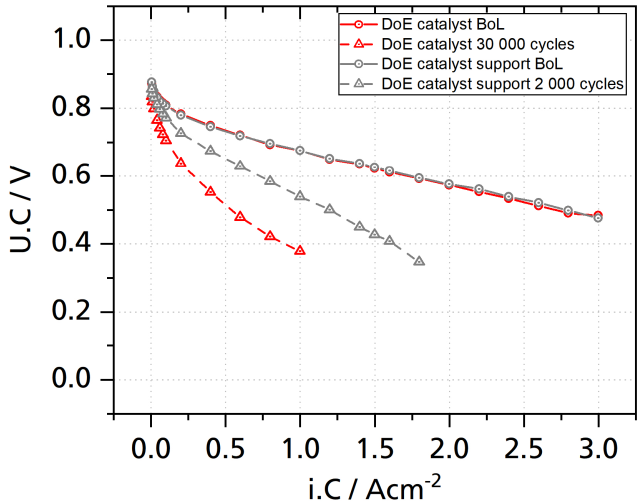
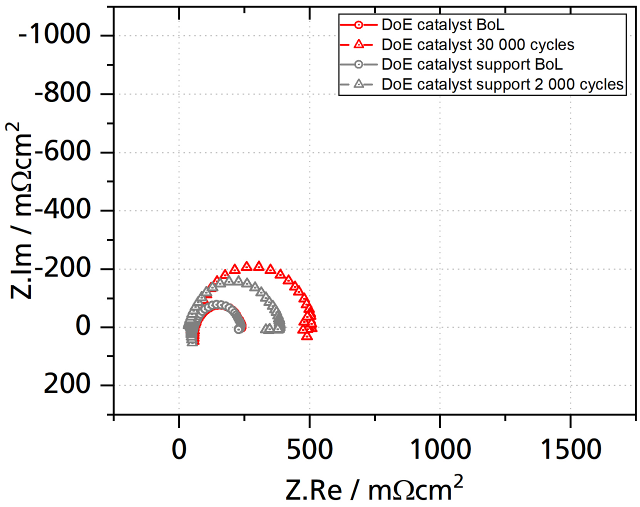


Figure 15: Polarization curve and EIS in conditions CatInHot





. Figure 16: Polarization curve and EIS in conditions CatOutHot

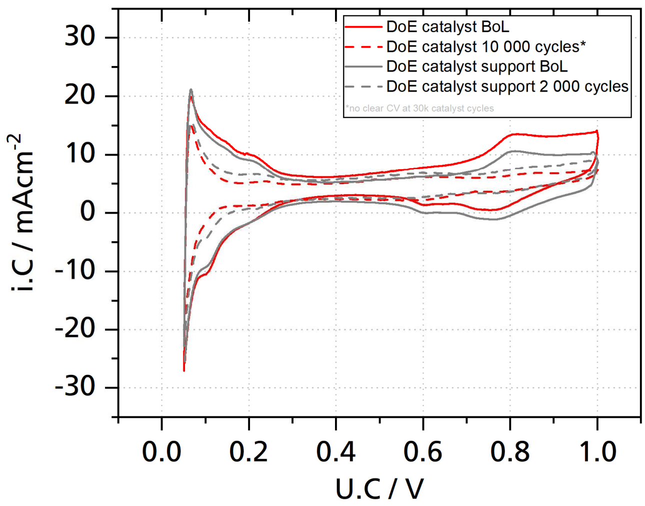


Figure 17: Cyclovoltammetry BoL and EoT.

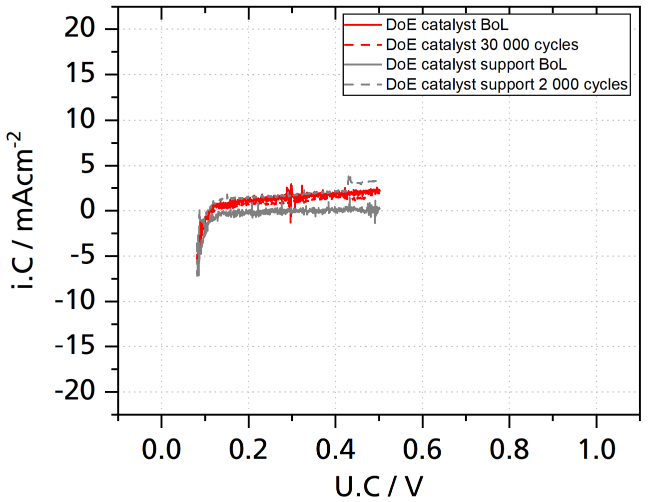


Figure 18: Linear Sweep Voltammetry BoL and EoT.

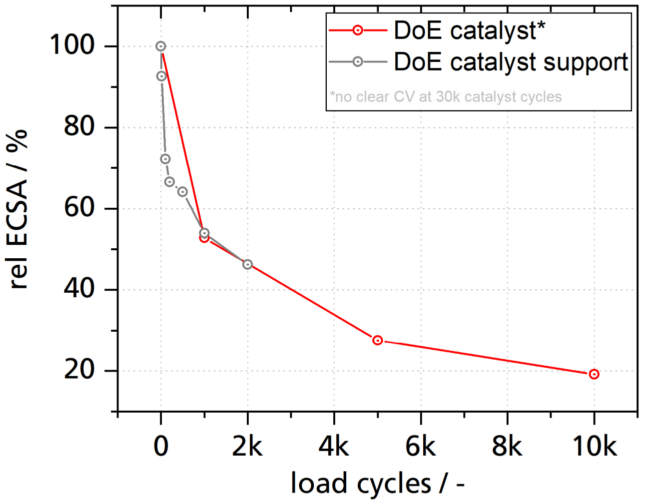


Figure 19: Relative losses in ECSA during ASTs.

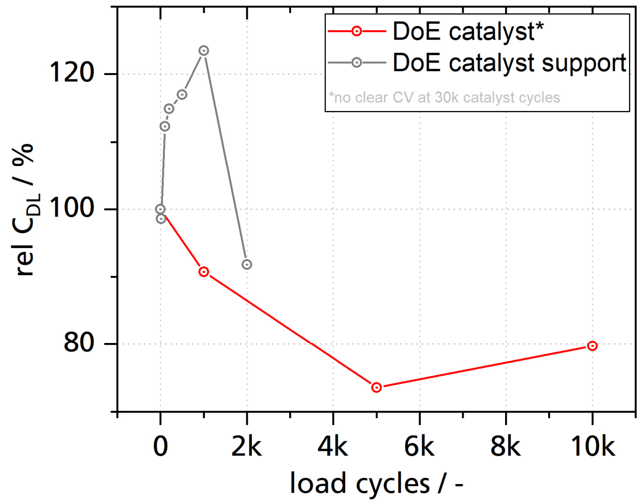


Figure 20: Relative losses in Double Layer Capacity during ASTs.

4.4 Comparison of JRC and Baltic test cell hardware

Remark: As the final test cell hardware of JRC is not available by August 2019 the final comparison is delayed. Nevertheless JRC and Fraunhofer ISE did some separate measurements with their respective test cell hardwares during the individual development phases mid of 2018. The results of these tests are presented below.

Within the tests presented below performed at JRC or Fraunhofer ISE, same material, a Gore CCM (0.1 / 0.4 $mg_{Pt}cm^{-2}$, 18 µm membrane) and similar operating conditions were used.

The test conditions were:

- Stoich 8/10 (An/Ca, min flow 0.2 Acm^{-2})
- T cell: 80°C
- RH: 100% (Anode and Cathode)
- P_{anode}(inlet): 250 kPa(absolute)
- $P_{cathode}$(inlet): 250 kPa(absolute) (test at ISE)
- $P_{cathode}$(inlet): 230 kPa(absolute) (test at JRC)

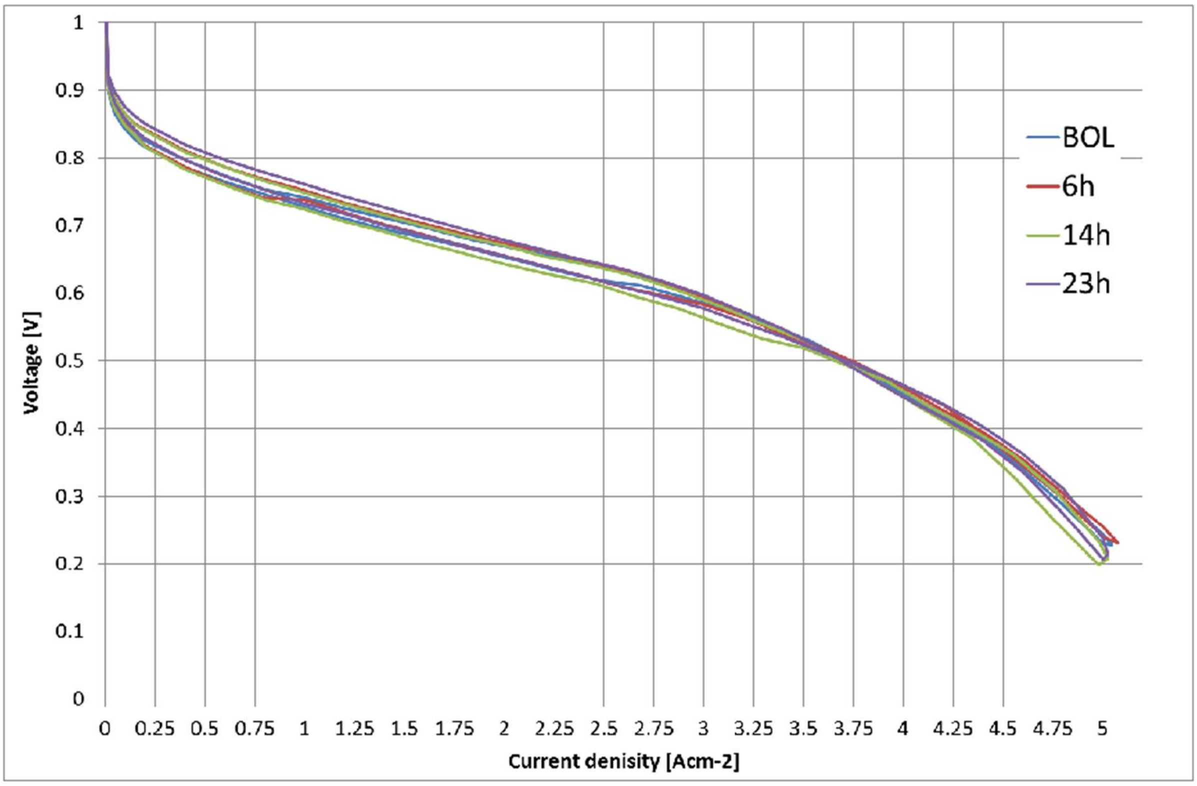


Figure 21: Comparison of polarization curves. Testing was done at JRC for JRC test cell hardware.

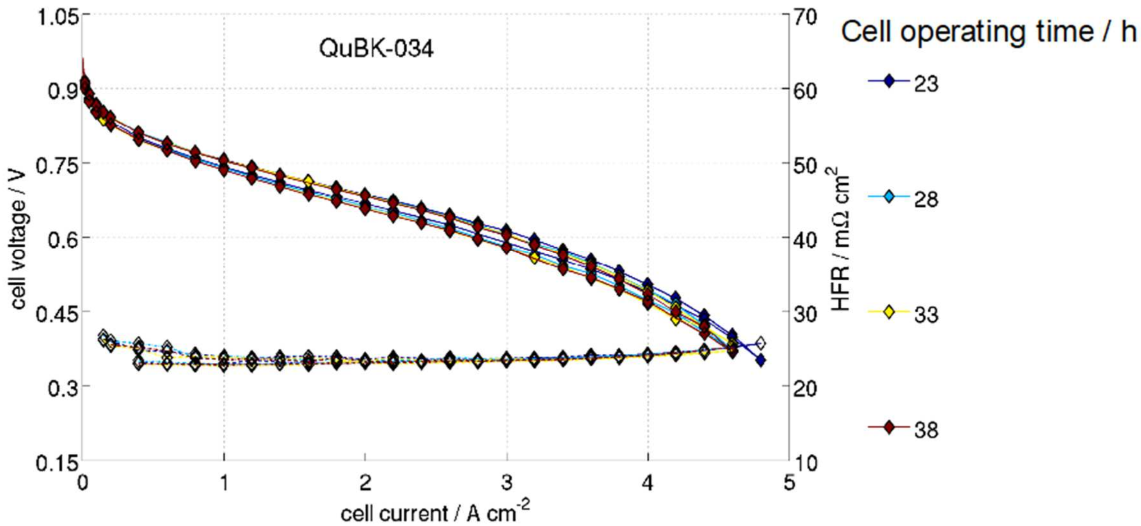


Figure 22: Comparison of polarization curves. Testing was done at Fraunhofer ISE for Baltic hardware.

As both test cell hardwares showed similar results the consortium decided to use both hardwares for the project.