Sustainable SoluTions FOR recycling of end-of-life Hydrogen technologies

Deliverable D2.3

Report on the evaluation of MEA including recycled materials in small single cell of PEMFC

Document Details

Due date	M28 (30 April 2023)
Actual delivery date	
Lead Contractor	CEA_Christine Nayoze-Coynel
Version	
Prepared by	CEA_Christine Nayoze-Coynel
Input from	
Reviewed by	HENSEL IDO-Lab EKPO ENVIPARK

Document Details

x PU - Public

CO - Confidential, only for members of the consortium (including the EC)

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation program, Hydrogen Europe and Hydrogen Europe Research.

Abbreviations

CCM	Catalyst Coated Membrane
CEA	Commissariat à l'Energie Atomique et aux Energies Alternatives
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
ECSA	Electro Chemical Surface Area
GDL	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
PEMFC	Polymer Exchange Membrane Fuel Cell
Pt	Platinum
$R_{H^+/cathode}$	Protonic resistance in the cathode
$R_{H^+/mb}$	Protonic resistance in the membrane
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Contents

Figures table:

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Annex table:

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Executive Summary

In the frame of BEST4Hy project, CEA must evaluate the recycled components in Membrane Electrode Assembly (MEA), to implement closed loop recycling especially on the recycled Pt in the catalyst. The catalyst (Pt/C) containing the recycled Pt (in short, hereinafter: the recycled catalyst) has been synthesized at CEA with the polyol reduction synthesis using the recycled Pt salt coming from HENSEL & IDO-Lab partners, from aged MEAs coming from EKPO. The target of the project for the integration of the recycled Pt into new MEA is 90% reaching 80% of performances of a MEA manufactured with commercial components, evaluated @ 1A/cm² in 25cm² single cell.

The deliverable 2.3 is a report concerning the evaluation of MEA including recycled materials in small single cell of PEMFC; the material concerned for the recycling here is the Pt that is transformed in Pt/C catalyst after synthesis to be usable into a MEA of PEMFC.

To compare the performances of MEA integrating recycled catalyst, a composition of reference MEA has been defined at the beginning of the project, as the test protocol discussed between EKPO and CEA. The reference MEA, named Best4Hy reference MEA, is manufactured by CEA, including commercial components (catalyst, ionomer and membrane) for the electrochemical core named the Catalyst Coated Membrane (CCM) with the Gas Diffusion Layer (GDL) coming from EKPO. The way of manufacturing the MEA has been adapted especially concerning the process deposition of the electrodes, depending on the available quantity of catalyst synthesized and on the quality of the catalyst obtained (Pt crystallites size).

To evaluate the catalyst and to reach the target, different studies have been done, such as the impact of the nature of the Pt salt used during the synthesis, the cathode catalyst loading (expressed in mg_{Pt/cm^2}), the use of catalyst with 5nm Pt crystallites size and the ratio of the ionomer on the carbon (I/C) in the inks. The characterization done on the MEAs to evaluate the performances, and thus the quality of the recycled Pt/C catalyst, are the determination of the polarizations curves (the voltage in function of the current density) and the electrochemical characterizations like the Electrochemical Impedance Spectroscopy (EIS) and the Cyclic Voltammetry (CV). These characterizations allowed selecting an ink composition giving the performance closer to the Best4Hy reference MEA. An ink composition with a ratio of I/C=0,87 with recycled catalyst on both side (anode & cathode) permitted to reach 96% of performance @ 1A/cm² vs BEST4Hy reference MEA in 25cm² single cell in an operating condition coming from stack operation. This selection is linked to the *MS5_Selection of MEA composition including recycled materials* for large scale CCM manufacturing.

As the recycled components must be evaluated in a short stack at EKPO, around 10 CCM will be manufactured for EKPO stack design using the ink composition selected in the MS5. EKPO will evaluate these CCM in a short stack using a specific test protocol.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Introduction

The aim of the BEST4Hy « sustainaBlE SoluTions FOR recycling of end-of-life HYdrogen technologies » project is to recycle end of life hydrogen technologies, Polymer Exchange Membrane Fuel Cell (PEMFC) and Solid Oxide Fuel Cell (SOFC), targeting critical raw materials like platinum (Pt) for the PEMFC, and rare earth element, such as cobalt (Co) and nickel (Ni) for the SOFC.

In the frame of BEST4Hy project, especially in the *WP2_ Characterization and evaluation of recycled materials in single cell and stack PEM configuration* in which CEA is leader, HENSEL & IDO-Lab and EKPO partners, CEA must:

- Characterize the recycled materials like the recycled Pt salts (coming from HENSEL & IDO-Lab partners) and the recycled catalyst, to evaluate their quality.
- Transform the recycled Pt salt into the catalyst Pt/C usable in a MEA for PEMFC. The aim is to implement a closed loop recycling of Pt in the recycled catalyst by introducing it into new MEAs.
- Integrate the recycled components into catalytic inks. In the project, the aim is to recycle Pt and ionomer and introducing them into new MEA. The recycled ionomer in dispersion obtained with the alcohol dissolution process could not be included into MEA because of some difficulties have been encountered in determining the quality of the material recovered (cf. deliverable D1.4). Thus, in this deliverable, we only speak about the recycled catalyst.
- Manufacture MEAs with the recycled catalysts, from small single cell (1.8cm² and 25cm²) to large CCM design (190cm²).

CEA has received different batches of recycled Pt salt, namely ammonium hexachloroplatinate $(NH_4)_2PtCl_6$ salt, from HENSEL & IDO-Lab partners, to be evaluated in different synthesis. After having tested three types of synthesis, the recycled catalyst has been finally synthesized with the polyol reduction synthesis using recycled Pt salt. The choice of the polyol reduction synthesis explained in deliverable *D2.1_Report on the catalyst synthesis at lab scale and quality testing of the recycled material*, allowed to up-scale this synthesis, for which the details are provided in deliverable *D2.2_Report on the synthesis up-scale*. Thus, around 16g of Pt/C catalyst have been synthesized, the required quantity to manufacture large CCM to EKPO stack design.

In the first part, this document describes:

- The reference MEA composition,
- The main results in term of recycled catalyst characterizations highlighting the quality of the synthesized catalyst,
- The MEA manufacturing and,
- The test protocols used to test the MEA, defined in collaboration between EKPO and CEA.

A reference ink composition has been defined to compare the MEAs including recycled catalyst, all the others components being commercial (ionomer, membrane and GDL which is a reference from EKPO).

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

In the second part, this document presents in more details the results obtained in the characterization of small single cells manufactured including recycled catalyst in MEAs. Different studies have been carried out to evaluate the MEAs performance, and thus the quality of the ink formulation:

- The impact of the nature of the Pt salt used during the synthesis,
- The cathode catalyst loading (expressed in mg_{Pt/cm^2}),
- The use of catalyst with 5nm Pt crystallites size and,
- The ratio of the ionomer on the carbon (I/C) in the inks.

All the MEAs are evaluated in term of performances and some electrochemical characterizations have been performed. The result of these evaluations lead to select an optimized ink composition to be used for the large CCM manufacturing for EKPO. This selection corresponds to the milestone *MS5_Selection of MEA composition including recycled materials*.

CEA will have to manufacture 10 CCM to stack design with the optimized ink formulation corresponding to Deliverable *D2.4_ 10 CCM including recycled materials for short stack assembly*. These CCM will be tested at EKPO in a short stack.

To have a better reader of this document, find below a list of the definition of the types and content of MEAs and types of catalyst manufactured and how we write them shorter in the deliverable:

Table 1 correspondence between the MEA and catalyst content and their way of writing in the document

Type and content of MEAs and catalyst	Referred as to
BEST4Hy reference MEA: manufactured at CEA with commercial components (catalyst, ionomer, membrane, GDL)	B4H reference MEA
MEA assembled with commercial components (CCM and GDL) coming from EKPO	EKPO MEA
Catalyst synthesized by polyol reduction with recycled Pt salt	Recycled catalyst
Catalyst synthesized by polyol reduction with recycled Pt salt with Pt crystallites size between 3 and 4nm	Optimized recycled catalyst

3 MEA remanufacturing & test protocol

3.1 Reference MEA

CEA must manufacture MEAs at 25cm² scale and to EKPO MEA design. Different type of MEAs will be manufactured: the project reference one and the one including the recycled catalyst, which has been synthesized from recycled Pt salt from aged MEA.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

The B4H reference MEA has been defined taking into account the composition of the EKPO MEA (using non-confidential data on this MEA) and the capability in term of catalyst synthesis at CEA:

Table 2 B4H reference MEA composition

Components	Reference	Parameter	Value
Catalyst	Tanaka TEC10V50E ≈ 50%Pt on Carbon Vulcan XC72	Anode Catalyst loading (mgPt/cm²)	0,1-0,15
		Cathode Catalyst loading (mgPt/cm²)	0,35-0,4
Ionomer	Nafion DE2020	I/C ratio	0,7
Membrane	Gore MX820.15 - PFSA	Thickness	15 µm
GDL	EKPO GDL	-	-

The commercial components have been chosen as closer as possible to the composition of the EKPO MEA and, for the catalyst, as closer as possible to the one that will be synthesized at CEA.

The reference electrodes are manufactured using the bar coater process deposition, like for the large CCM to EKPO stack design. The Catalyst Coating Decal technique is used. This technique consists in depositing first the electrodes on an inert support and then decal them on both side of the membrane by hot pressing to obtain the CCM. The addition of the GDL on each part of the CCM by hot pressing gives a full MEA.

3.2 Catalyst synthesis

In the project, three types of synthesis have been evaluated and the results are reported in *D2.1_Report on the catalyst synthesis at lab scale and quality testing of the recycled material*, leading to select the polyol reduction synthesis to be up-scaled. A report is dedicated to this up-scale, *D2.2_Report on the upscaling of the catalyst synthesis*. The recycled catalysts obtained with the polyol reduction synthesis and the commercial catalyst selected in the project have very similar characteristics. That is why this synthesis has been chosen as the one to be upscale. The target for the Pt crystallites size is between 3 and 4nm; the one for the wt.%Pt deposited onto the carbon is 40%.

The XRD technique has been used to evaluate the Pt crystallite size. The results are presented in the following figure. The size of the Pt crystallite is calculated using the FWHM (Full width at Half Maximum) on Pt peaks.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

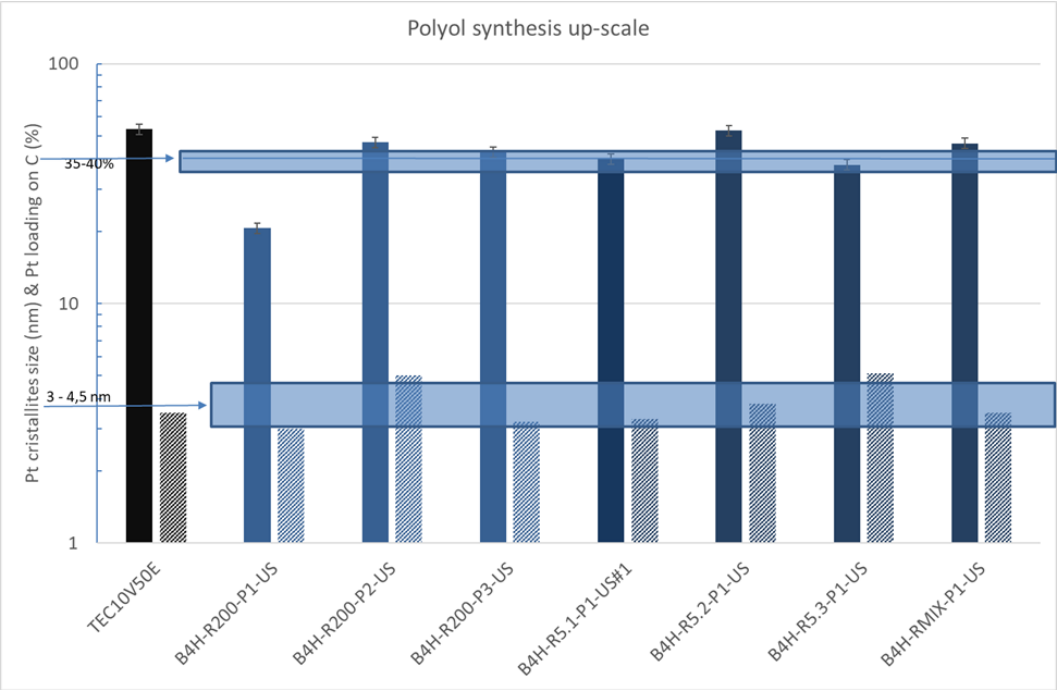


Figure 1: Pt crystallites size (nm) determined by XRD and Pt loading (wt.%) deposited onto C determined by UV spectroscopy

At the total, around 20g of catalyst has been synthesized with the polyol synthesis:

- 4g of catalyst has been synthesized at lab scale and pre up-scale (quantity <2g of catalyst); which the result of the Pt crystallites size and the Pt loading are represented in light blue
- 16g of catalyst has been synthesized at the up-scale, which the result of the Pt crystallites size and the Pt loading are represented in dark blue. This quantity of catalyst is dedicated to the manufacturing of the large CCM.

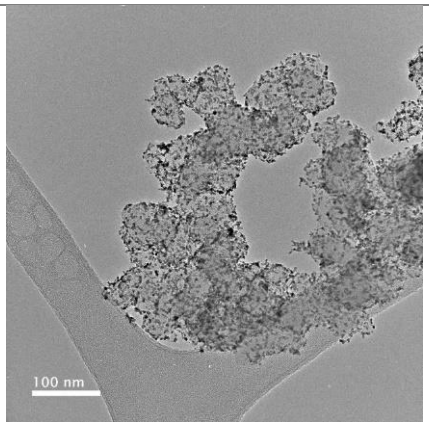
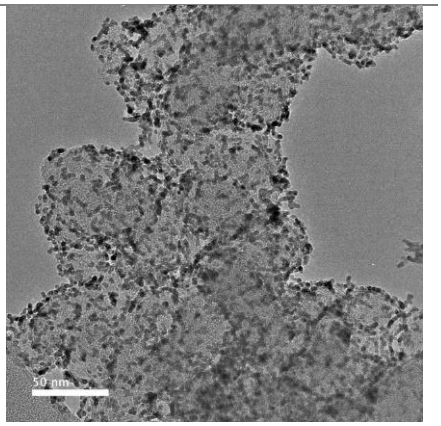
The crystallites Pt sizes coming from the up-scale are between 3 and 4nm, close to the one obtained in small scale, and close to the reference commercial catalyst. They are globally in the target, excepted for one up-scaled catalyst, for which the Pt crystallites size is around 5nm. Globally, these results lead to conclude that the parameters used during the up-scale of the polyol reduction synthesis are optimized.

Thus on the total of 16g of catalyst synthesized and which must be integrated into the large CCM, only 12g are available with optimized Pt crystallites size (between 3 and 4nm) and 4g with non-optimized Pt crystallites (around 5nm). This last batch will be evaluated in MEA to see if it is relevant to use such a type of catalyst in MEA, in the case of no sufficient catalyst with optimized Pt size is available for the large CCM manufacturing. The results are presented in section 4.5.

Some microstructural characterizations made using the Transmission Electron Microscopy (TEM) have been done on catalyst synthesized at different up-scale of polyol reduction synthesis to evaluate the distribution of the Pt on the Carbon. The table below shows some example of pictures of the microstructure of catalyst with optimized Pt crystallites size and Pt loading.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Table 3 Example of TEM pictures of a catalyst synthesized with the up-scaled polyol reduction (4g) synthesis with optimized Pt crystallites size and Pt loading

R5.1-P1-US#1 by polyol reduction synthesis (up-scale 4g)	
Pt Crystallite size (nm)	3.3
Pt loading on C (%)	40,1 ± 1,8
	

No specific influence on the microstructure can be observed between a pre-upscale (2g of catalyst) and the up-scale (4g of catalyst). The characteristics observed on the recycled synthesized catalyst are close to the commercial catalyst. The Pt is well dispersed onto the C, with small Pt crystallites (between 3 and 4nm). This proves that the parameters for the up-scale synthesis are optimized, and the catalyst can be used in the ink formulation to reach the performance of 80% vs B4H reference MEA and to manufacture the large CCM to EKPO stack design.

The evaluation of the recycled catalyst has been done in different size of MEAs.

3.3 MEA remanufacturing

Two different sizes of MEA are proposed, depending on the quantity of available recycled catalyst. The Figure 2 represents a 1.8cm² single cell for small quantity of catalyst (<0.5g) and the Figure 3 a 25cm² single cell for higher quantity (>0.5g).

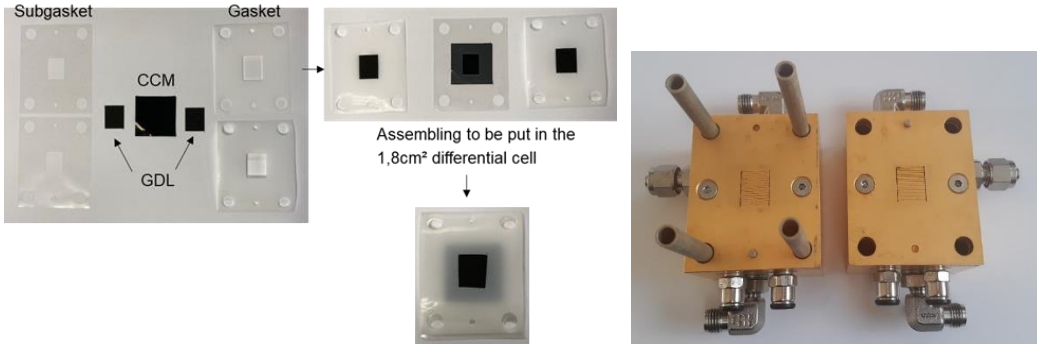


Figure 2 Homemade differential cell setup characterization

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

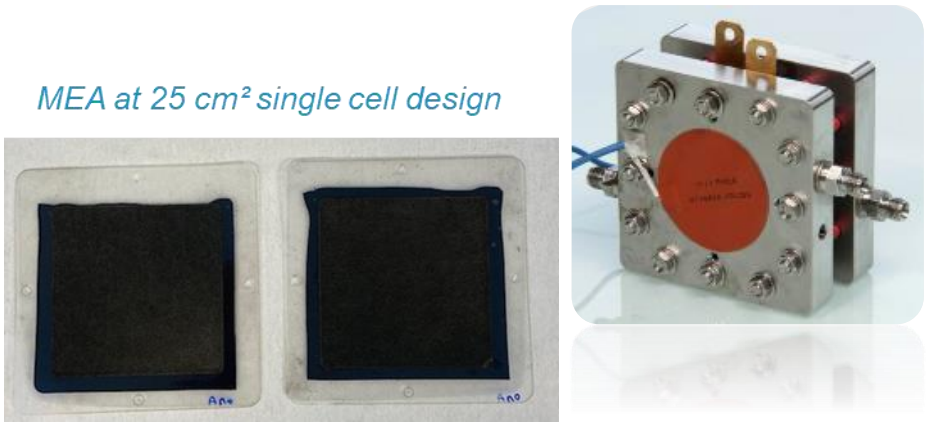


Figure 3 25cm² single cell design

Different techniques for the electrode deposition are used, depending on the quantity of the catalyst available:

- The spray technique for the study of the recycled catalyst when small quantities of catalyst are obtained (<0.5g) during the catalyst synthesis at lab-scale. In this case, the recycled catalyst is evaluated only on the cathode side.
- The bar coater technique for
    - The reference electrode,
    - The study of the recycled catalyst synthesized with the pre-upscale (≈1g and ≈2g) and the up-scaled polyol reduction (>4g).
    - The manufacture of the large CCM to EKPO stack design

All the electrodes for the small single cell and the large CCM are manufactured using Catalyst Coating Decal technology, i.e., the electrodes are first deposited on an inert support and then decaled onto the membrane by hot pressing. The full MEAs are obtained by adding the GDL by hot pressing on each side of the CCM.

3.4 Test protocol

CEA proposed a “strategy” to test the different MEAs, as represented in the Figure 4.

The aim is to test the MEA first in a differential cell of 1.8cm², in a very small design. The principle of testing this homemade single cell is based on the electrochemical evaluation of MEA under three homogeneous operating conditions using high stoichiometries. This evaluation on single cells will allow making an easy comparison between pristine and recycled Pt salt based on electrodes with low amount of catalyst coming from lab-scale synthesis (<0.5g of catalyst).

As the recycled catalyst obtained by the microwave assisted polyol reduction synthesis and by thermal reduction in reductive atmosphere synthesis had not satisfactory characteristics, only the recycled catalyst coming from the polyol reduction synthesis have been tested in 1.8cm² single cell. This permitted to optimize the parameters of the polyol reduction synthesis, to evaluate in the same time the impact of the nature of the Pt salt used (recycled vs commercial), to validate the quality of the recycled catalyst coming from the different up-

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

scale synthesis and to evaluate the impact of the modification of the ink formulation. This allowed making a pre-selection of the recycled catalyst using a little quantity of catalyst.

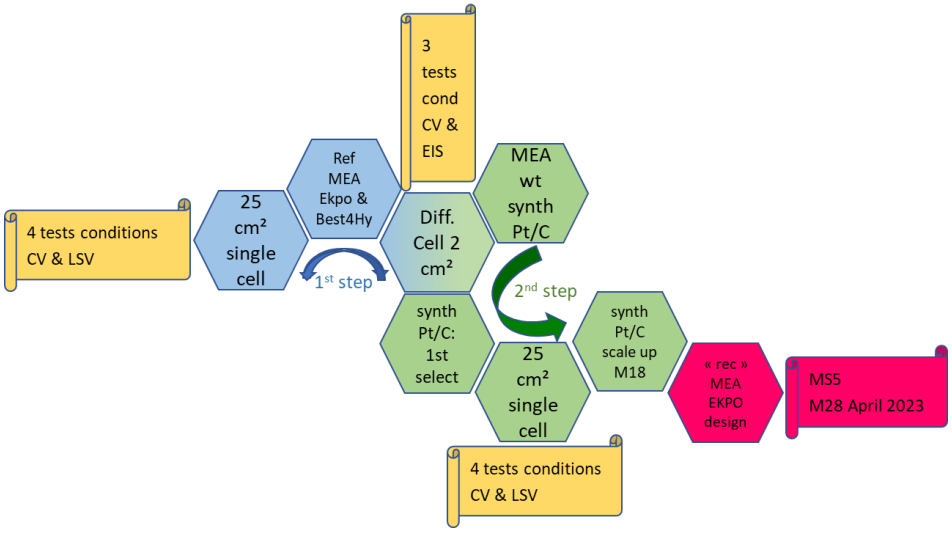


Figure 4 "strategy" to test MEAs at different design

Three operating conditions and characterizations like the Electrochemical Surface Area (ECSA) and Electro Impedance Spectroscopy (EIS) are proposed for the test in 1.8cm² differential cell. The protocol is the following:

Table 4 Operating conditions for 1.8cm² MEAs

Conditions	Cell	Pressure		Dew point / Relative Humidity				Stochiometry		Gas		Characterization
	T_cell	P_An_Out	P_Ca_Out	T_DP_An	RH_An	T_DP_Cath	RH_Cath	λ (St)_An	λ (St)_Cath	An.	Cath.	
	°C	Bar abs	Bar abs	°C	%	°C	%	-	-			
Break-in	70	1,1	Atm (outlet)	70	100	70	100	~ 50 @ 1A/cm²	~ 50 @ 1A/cm²	H2	air	0,4V / 0,6V / OCV; 30 cycles
1	80	1.5	1.5	74	80	74	80	~ 50 @ 1A/cm²	~ 50 @ 1A/cm²	H2	air	Pol Curve, PEIS
1bis	80	Atm (outlet)	Atm (outlet)	74	80	74	80	500 NmL/min	500 NmL/min	H2	N2	ECSA, IH2, PEIS
2	80	1.5	1.5	64	50	64	50	~ 50 @ 1A/cm²	~ 50 @ 1A/cm²	H2	air	Pol Curve, PEIS
3	60	1.5	1.5	64	> 100	64	>100	~ 50 @ 1A/cm²	~ 50 @ 1A/cm²	H2	air	Pol Curve, PEIS
4	30	Atm (outlet)	Atm (outlet)	35	> 100	35	>100	500 ml/min	500 ml/min	H2	N2	ECSA, IH2, PEIS

The recycled catalyst, coming from pre-upscale polyol reduction synthesis has been tested in 25cm² in a second step, under four operating conditions, using technic stoechiometries. These tests in 25cm² permitted to evaluate the performance of the B4H reference MEA, the EKPO MEA and to study the impact of the modification of the ink composition in realistic operating conditions. Based on the comparison in performances, one ink composition integrating recycled catalyst has been selected to manufacture CCM at EKPO design.

The catalyst the more promising has been evaluated in 25cm² using the following test protocol:

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Table 5: operating conditions for 25cm² MEAs

Conditions	Conditions	Cell T°C	Pressure		Dew point / Relative Humidity				Stoechimetry		Gas		Caracterization
		T_cool_in_set (cell T°)	P_An_in_set	P_Ca_in_set	T_DP_An_set	HR_An	T_DP_Ca_set	HR_Cat	λ (St)_An_set	λ (St)_Ca_set	Anode	Cathode	
		°C	bar	bar	°C	%	°C	%	-	-			
	break-in	70	1,1	1	70	100	70	100	Flow @ 1,5-2A/cm²	Flow @ 1,5-2A/cm²	H2	air	0,4V / 0,6V / OCV; 30 cycles
1	Automotive cond.	80	1,5	1,5	63	50	63	50	1,5	2	H2	Air	Pol Curve
2	Europe cond.	80	2,5	2,3	63	50	50	30	1,3	1,5	H2	Air	Pol Curve
3	Cond « high current density » _1,95A/cm²	75	2,5	2,4	54	40	70	82	1,5	1,7	H2	air	Pol Curve
4	Cond « low current density » _0,11A/cm²	65	1,3	1,0	52	55	60	82	1,5	2,6	H2	air	Pol Curve
5	CV	60	2	2	55	80	55	80	500 ml/min	500 ml/min	H2	N2	30-50 & 100 mV/s; tbd-0,95 V; 3 cycles
6	LSV	60	2	2	55	80	55	80	660 ml/min	660 ml/min	H2	N2	2 mV/s; 0,065-0,865 V; 1 cycle
7	EIS	60	2	2	55	80	55	80	660 ml/min	660 ml/min	H2	N2	EIS @ 0,4V

The conditions proposed by EKPO linked to the use in stacks were adapted to the use of the single cell test bench at CEA. Indeed, in stack, some parameters are variables during the polarization testing, for example stoichiometry, coolant T°C, dew point…, whereas the single cell test bench at CEA imposes constant parameters during this characterization.

In the final operating conditions, two conditions are derived from EKPO's ones, linked to the parameters obtained at different current density in stack (at high current density 1,95A/cm² and low current density 0,11A/cm²). The two other conditions are derived from CEA's standards to compare performance in specific normalized condition like automotive application and other one based of the EU Harmonized Automotive Reference Operating Conditions named European condition[1] in the table.

4 MEA performances

CEA manufactured MEAs at different design: 1.8cm² (for differential cell), 25cm² (technical cell) and at stack design (EKPO).

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

[1] European Commission, Joint Research Centre, De Marco, G., Malkow, T., Tsotridis, G. et al., EU harmonised test protocols for PEMFC MEA testing in single cell configuration for automotive applications, Publications Office, 2015, https://data.europa.eu/doi/10.2790/54653

4.1 List of MEA manufactured and tested

The following table summarizes the MEAs manufactured during the project, in 1.8cm² and 25cm², leading to select the optimized ink composition. The green symbol signifies that the MEA has been tested, the red symbol identifies the ones that have been discarded because they were scratched during testing due to a problem of the dedicated test station.

Table 6 MEA manufactured and tested at 1.8cm² and 25cm² integrating the EKPO components (EKPO MEA in orange), the commercial components (B4H reference MEA in blue) and the recycled catalyst synthesized by polyol reduction (green)

Mb	GDL	Anode process	Cathode process	Anode loading (mg/cm2)	Cathode loading (mg/cm2)	Comments	N°MEA	Cell Surface (cm²)	N°MEA	Cell Surface (cm²)
Gore 820.15	GDL Ekpo			0,1	0,5	EKPO CCM	A5535	1,8	A5525 A5526	25
Gore 820.15	GDL Ekpo	Bar coater	Spray	0,18	0,23	Anode ref; cathode com. catalyst	A5538 ✓	1,8		
Gore 820.15	GDL Ekpo	Bar coater	Spray	0,12	0,23	Anode ref; cathode B4H-C-Pt (Polyol-com Pt salt)	A5646 ✓	1,8		
Gore 820.15	GDL Ekpo	Bar coater	Spray	0,12	0,22	Anode ref; cathode B4H-R0h-Pt (Polyol-MEA 0h)	A5645 ✓	1,8		
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,12	0,51	Anode ref; cathode ref	A5556 ✓ A5588 ✓	1,8	A5534 ✓ A5605 ✓ A6017 ✓	25
Gore 820.15	GDL Ekpo	Bar coater	Spray	0,12	0,40	Anode ref; cathode B4H-C-P1 (Polyol-com Pt salt)	A5683 ✓	1,8		
Gore 820.15	GDL Ekpo	Bar coater	Spray	0,12	0,40	Anode ref; cathode B4H-R0h-P1 (Polyol-MEA 0h)	A5682 ✓	1,8		
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,121	0,42	Anode ref; cathode B4H-R200-P1-US I/C 0,57	A5712 ✓	1,8	A5711 ✓	25
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,121	0,39	Anode ref; cathode B4H-R200-P1-US I/C 0,67	A5719 ✓	1,8	A5718 ✓	25
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,11	0,34	Anode B4H-R200-P3-US I/C 0,77 cathode B4H-R200-P3-US I/C 0,77	A5811 ✓	1,8	A5807 ✗	25
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,12	0,46	Anode B4H-R200-P3-US I/C 0,87 cathode B4H-R200-P3-US I/C 0,87	A5812 ✓	1,8	A5808 ✓	25
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,17	0,44	Anode ref; cathode B4H-R200-P2-US (Pt 5 nm)	A5809 ✓	1,8	A5805 ✓	25
Gore 820.15	GDL Ekpo	Bar coater	Bar coater	0,14	0,51	Anode B4H-R200-P2-US (Pt 5 nm) ; cathode ref	A5810 ✓	1,8	A5806 ✗	25

Since the start of the *task 2.3_Remanufacturing of MEA* at M11 and the *task_2.4 Performance evaluation of recycled materials* at M13, the following types of MEAs at 1.8cm² and 25cm² scale have been manufactured:

- EKPO MEA: the commercial reference MEA from EKPO including both CCM and GDL from EKPO. CCM and GDL in this case, have just been cut and hot pressed to manufacture the full MEA.
- B4H reference MEA: the project reference MEA manufactured at CEA including commercial components, to have reference performances. The electrodes with commercial components have been manufactured at CEA, using the reference ink composition defined in section 3.1 and using the bar coater, the same process that will be used for large CCM manufacturing for EKPO in task 2.3.2.
- The MEAs with recycled catalysts: MEAs integrating recycled catalyst synthesized by polyol reduction synthesis using recycled Pt salt precursor from HRD.

The aim of the different MEA manufactured and compositions are to study:

- The performance of B4H reference MEA manufactured with commercial component vs performance of EKPO MEA manufactured with EKPO components (CCM & GDL)

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

- The impact of the nature of the Pt salt (recycled Pt salt vs commercial Pt salt) used to synthesize catalyst, on the performance,
- The effect on the performance of the cathode catalyst loading using recycled catalyst on the cathode side
- The impact of the size of the Pt crystallites on anode and/or cathode side
- The impact of the ink formulation to reach the target of 80% of performance vs B4H reference MEA, by adapting the ratio of ionomer on carbon (I/C).

The final aim is to select an optimized ink composition, leading to performance at least of 80% of performance at 1A/cm² in 25cm² vs B4H reference MEA and to use it to manufacture large CCM (190cm²) that will be evaluated in stack configuration at EKPO in task 2.4.2.

In the following sections, to have a clearer presentation of the results in the core of the document, all the polarization curves presented are compared in one condition only per type of single cell; the curves under the other testing conditions are shown in Annex 2 to Annex 6. The conditions are the following:

- In 1.8cm²: cond 3: 60°C_1.5bara_>100%HR_H2 air (cf. Table 4);
- In 25cm²: cond 3: 75°C_Pa 2.5 bara-Pc 2.4 bara_40HRa-82HRc_Sta 1.5-Stc 1.7_H2-air (cf. Table 5). This condition is derived from EKPO stack operation specs.

It is important to notice that the same trend is observed in all the testing conditions, if a MEA has higher performance compared to another one, it is true in all the conditions. The condition 3 for the 2 types of cell (1.8cm² and 25cm²) give the best performance, compared to other 3 conditions; that's why it has been decided to show in the main core of the deliverable only the conditions 3.

In the test protocol described in paragraph3.4, some electrochemical characterization are done, e.g. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltametry (CV). The method of calculation of some indicators such as resistance of the membrane is presented in Annex 1.

4.2 Comparison between BEST4Hy reference MEA vs EKPO MEA

CEA made the reference project MEA with commercial components, following the composition described in Table 2. The performance of the project reference MEA has been compared to a MEA with EKPO components (GDL and CCM). The MEA considered in this study are:

- For 1.8cm² single cell: A5535_EKPO MEA, A5556 and A5588_B4H reference MEA
- For 25cm² single cell: A5526_EKPO MEA and A5605__B4H reference MEA

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Their compositions are visible in the Table 6.

Results in 1.8cm²

The polarization curves in 1.8cm² in condition 3 (the others visible in the Annex 2) show that the performance of EKPO MEA is higher than the B4H reference MEA. This difference is explained by a better protonic conductivity at 30°C_Pa_100%RH for EKPO MEA, with a limitation of the gas diffusion for B4H reference MEA.

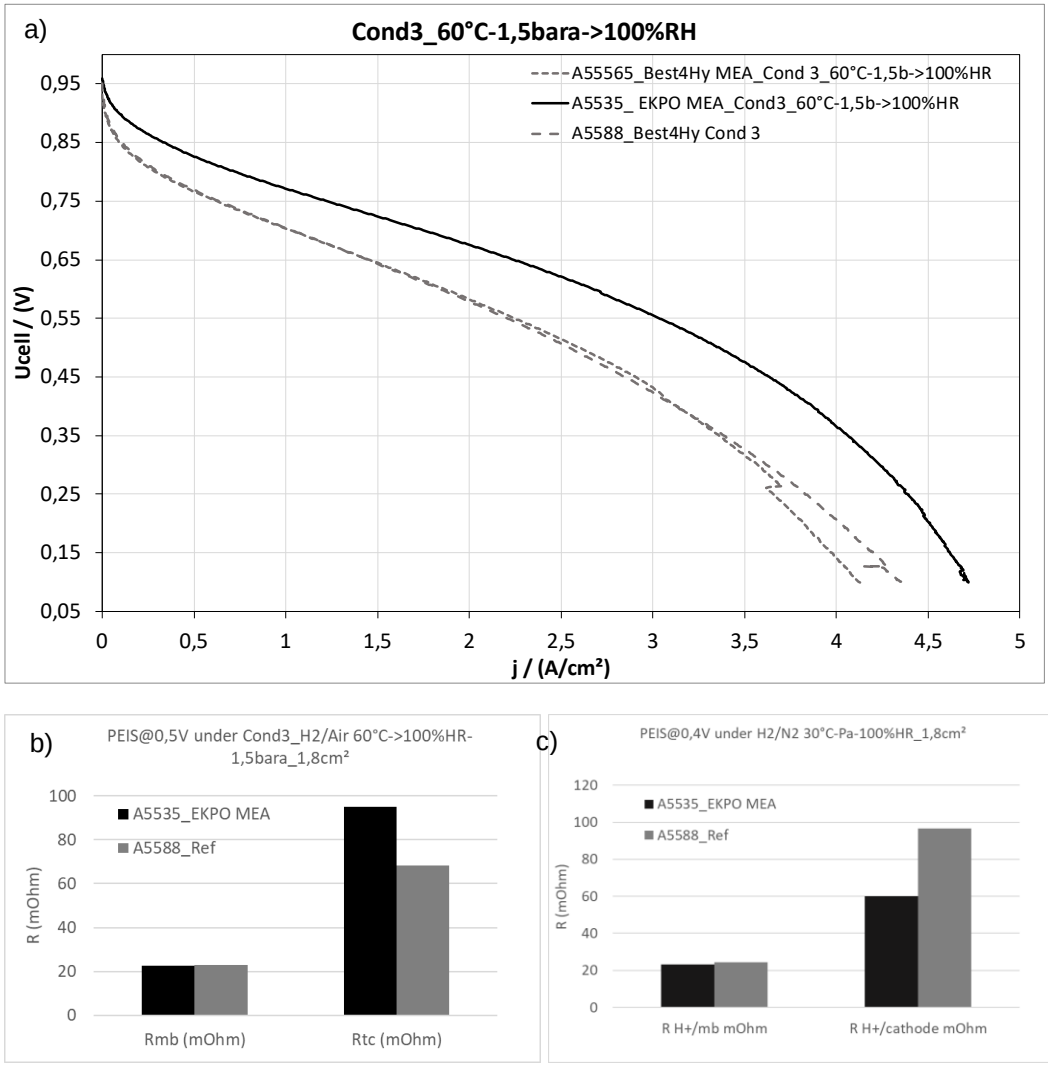


*Figure 5: comparison in 1.8cm² single cell between the B4H reference MEA (A5556 and A5588) represented in the grey dotted line and the **EKPO MEA (A5535)** represented in the black full line, in 1.8cm² single cell; a) in performance in cond3; b) PEIS@0.5V under H_2/air-Cond3; c) PEIS@0.5V under H_2/N_2 –cond4*

The polarization curves show a good reproducibility of the B4H reference MEA represented in grey dotted line.

The ECSA has been calculated from the curves obtained with the cyclic voltammetry (CV) experiment. The calculation of the ECSA (in cm^2_{Pt}/cm^2_{geo}) uses the specific charge of the Pt for the hydrogen adsorption of 210µC.cm^{-2}. However, the catalyst used in the EKPO MEA is a bi-metallic catalyst, i.e Pt + other metal deposited on Carbon. After a research in the literature, no specific value exists for this type of catalyst; the value commonly used is

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

210µC.cm^{-2}. Thus, the calculated values for the EKPO MEA give an idea about the active surface area. Moreover, for EKPO MEA, the experiment of the CV has not been realized in the same condition (due to a problem during the test) as the B4H reference MEA (curves presented in Annex 2). The minimum limit potential (Ei mV) for the potential ramp for the CV is not the same, leading to make a wrong comparison with B4H reference MEA, because the area of the integration is not the same. This explains why the comparison of the ECSA between the MEAs are not possible.

However since the capacitive band is higher for EKPO's MEA we can deduce that a different Carbon has been used in the cathodes of the two MEAs.

The value of the ECSA calculated for the B4H reference MEA are represented in the following figure:

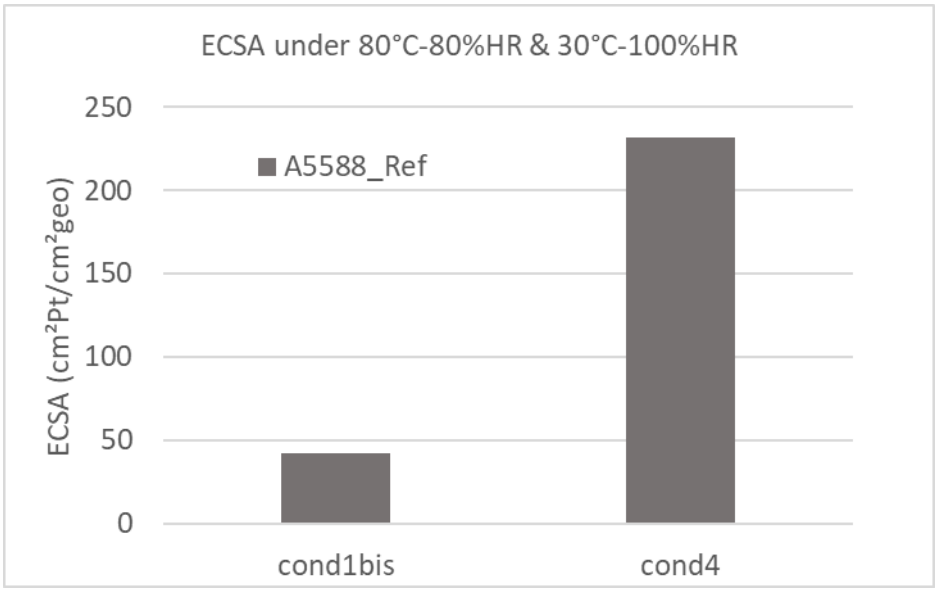


Figure 6 ECSA results of B4H reference MEA in 1.8cm² single cell

Results in 25cm²

The performances obtained in 25cm² show that the B4H reference MEA has performances close to the EKPO MEA, with an intersection of the curves at 1,6A/cm², point from where the B4H reference MEA has higher performances. Whatever the conditions, there is an intersection between 1A/cm² and 1.5A/cm²; for higher current densities, the B4H reference MEA has higher performances compared to EKPO MEA.

This performance can be explained by a protonic resistance in the cathode slightly lower (i.e., better conductivity of H_2 in the cathode) compared to EKPO MEA. The protonic resistance in the membrane is also slightly lower for the B4H reference MEA at 60°C-2bara-80%HR (H_2/N_2). The calculation of the ECSA of EKPO MEA is just done here as an estimation due to the same reason given in the previous paragraph concerning the value of the specific charge. However, as the minimum limit potential (Ei mV) is the same for the two MEAs, we can "compare" these MEAs. Finally, the ECSA of the BEST4Hy reference MEA has similar value compared to EKPO MEA's, maybe slightly higher. This observation can explain the close performances between the BEST4Hy reference MEA and the EKPO

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

MEA. The result of the performances are interesting because a home-made MEA can have similar performance compared to a commercial MEA.

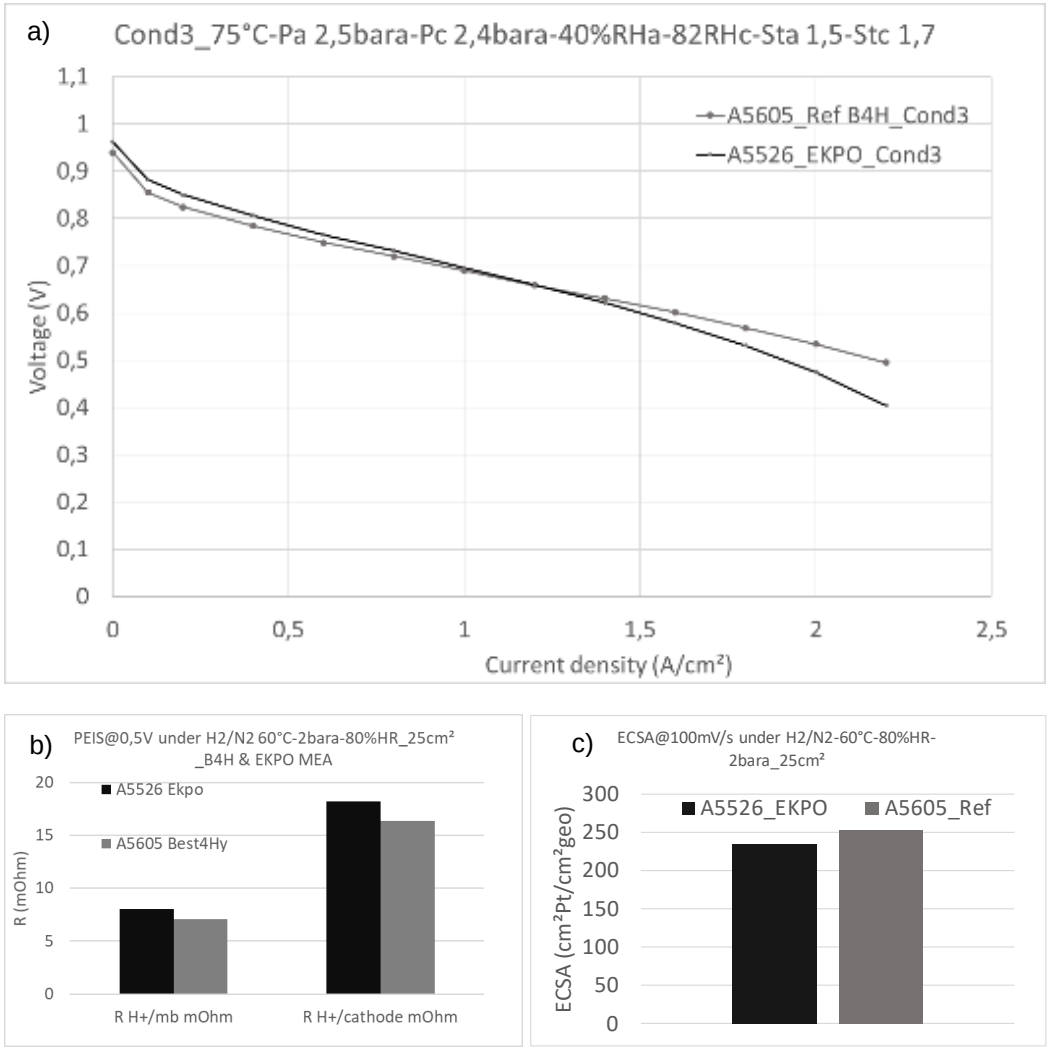


*Figure 7: comparison between the B4H reference MEA (A5605) and the **EKPO MEA (A5526)** in 25cm² single cell. a) in performance in cond3; b) PEIS@0.5V under H_2/air-cond3; c) ECSA@100mV/s under H_2/N_2 –cond5*

For the next sections, all the MEAs will be compared to B4H reference MEA:

- A5588 for the 1.8cm² single cell and,
- A5605 for the 25cm² single cell.

4.3 Impact of the nature of the Pt salt precursor

The first MEAs integrating recycled catalyst using polyol reduction synthesis have been manufactured using the spray as process deposition for the electrode; a low catalyst loading was used due to the low quantity of catalyst available obtained during the first catalyst synthesis, mainly not to waste catalyst material. The cathode catalyst loading considered in this study is 0.23mg_{Pt/cm^2}. The recycled catalyst has been introduced on the

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

cathode side, the anode side being the reference anode with commercial components with a loading of 0.12mg$_{Pt/cm^2}$.

The MEAs considered in this study are tested only in 1.8cm² single cell:

- MEA with catalyst synthesized with commercial Pt salt A5646
- MEA with recycled Pt salt (0h MEA) A5645, compared to
- a MEA manufactured with commercial components A5588

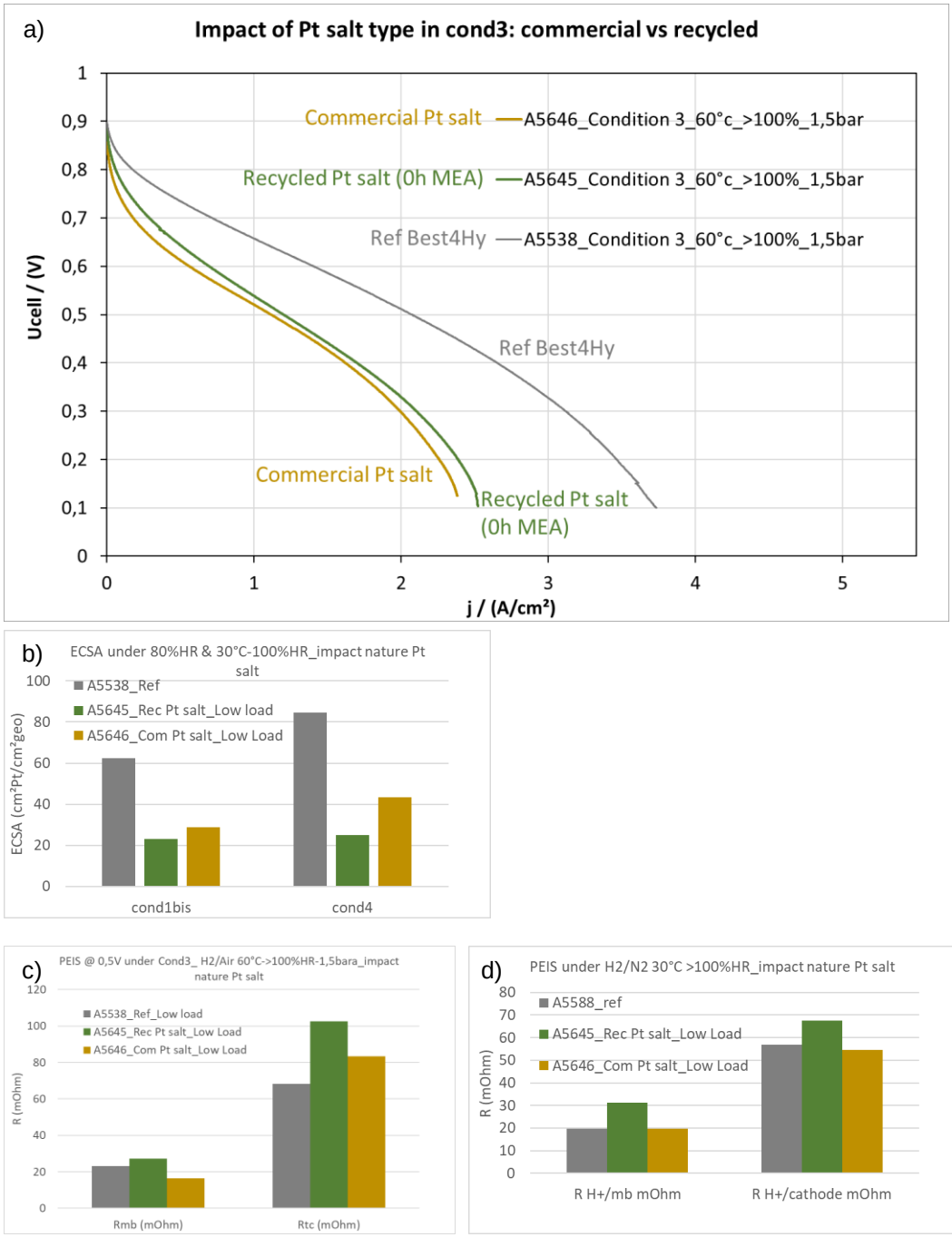


Figure 8: comparison of MEAs with catalyst synthesized with commercial Pt salt (A5646), recycled Pt salt (A5645), compared to a MEA manufactured with commercial components (A5588); in 1.8cm² single cell & 0.23 mg Pt/cm² on the cathode side; a) polarization curves in Cond3 b) ECSA@100mV/s; c) PEIS@0.5V in Cond3; d) PEIS@0.4V in H_2/N_2-cond4

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Comparison of MEA manufactured with catalyst synthesized with recycled Pt salt vs MEA manufactured with catalyst synthesized with commercial Pt salt:

The performances obtained with the MEA with catalyst synthesized with recycled Pt salt (0h MEA) are slightly higher than the MEA with catalyst synthesized with commercial Pt salt. This difference is much marked in the condition 2 which the performance are visible in the Annex 3. This difference in term of performances is also visible in the Figure 9: comparison of MEAs with different catalyst loading on the cathode side in 1.8cm² single cell a) polarization curves in cond3-60°C-1.5bara-100%RH; b) ECSA@100mV/s in cond1bis and cond4; c) relation between the ratio of the ECSA and the ratio of catalyst loadingFigure 9 in which it can be seen that the performance of the MEA with recycled Pt salt is higher compared to the MEA with commercial Pt salt, whatever the condition, for a higher catalyst loading (0.4mg_{Pt/cm^2}).

Whereas the ECSA of the MEA with catalyst synthesized with recycled Pt salt is lower compared to the MEA with catalyst synthesized with commercial Pt salt, and the R_{ct} (charge transfer resistance), $R_{H^+/mb}$ and $R_{H^+/cathode}$ (protonic resistance in the membrane and in the cathode) are higher, the performance are higher. The results of this electrochemical characterization are not coherent with the trend of the performances. No specific link can be done neither with the purity of the catalyst synthesized with the polyol reduction synthesis because the size of the Pt crystallites and the Pt loading (on carbon) are in the target.

What we can keep in mind is that the performance of MEA with catalyst synthesized with recycled Pt salt (0h MEA) are slightly higher than the MEA with catalyst synthesized with commercial Pt salt, in all the conditions tested and whatever the catalyst loading (0.23 mg_{Pt/cm^2} and 0.4mg_{Pt/cm^2}).

Comparison of MEA manufactured with catalyst synthesized with polyol reduction synthesis (recycled and commercial Pt salt) vs MEA manufactured with commercial components:

The performances of MEA integrating synthesized catalyst (with recycled and commercial Pt salts) are significantly lower compared to those of the MEA manufactured with commercial components. Indeed, their electrochemical surface area (ECSA) are twice lower, the charge transfer resistance (R_{ct}) and the protonic resistance in the cathode ($R_{H^+/cathode}$) are higher, compared the MEA manufactured with commercial catalyst.

These results in 1.8cm² single cell highlight that it is possible to use recycled Pt salt as precursor for the catalyst synthesis, without significant limitations of performances compared to the use of commercial Pt salt; but with a strong impact compared to a MEA manufactured with commercial components.

The next steps consist in exploring the effect on performance of using higher catalyst loading on the cathode side using recycled catalyst.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

4.4 Impact of the cathode catalyst loading

MEAs with higher cathode catalyst loading have been manufactured with the same electrode deposition process, the spray, and with the same Pt salt batch used for the study of the type of the Pt salt. The recycled catalyst has been introduced on the cathode side, the anode being the reference one with commercial components with a loading of $0.12mg_{Pt/cm^2}$.

The MEAs considered in this study are:

- The reference MEA (A5588) with $0.4_{mgPt/cm^2}$
- MEA with catalyst synthesized with commercial Pt salt
    - A5646 with $0.23_{mgPt/cm^2}$
    - A5683 with $0.4_{mgPt/cm^2}$
- MEA with catalyst synthesized with recycled Pt salt
    - A5645 with $0.23_{mgPt/cm^2}$
    - A5682 with $0.4_{mgPt/cm^2}$

The compositions of these MEAs are visible in the Table 6.

Figure 9 and Annex 4 present the impact of the catalyst loading on the cathode side, at $0.23mg_{Pt/cm^2}$ in dotted line and $0.4mg_{Pt/cm^2}$ in continuous line, in $1.8cm^2$ single cell, using catalyst synthesized with commercial Pt salt (A5646 & A5683) and recycled Pt salt (& A5682), compared to the reference MEA (A5588) at high catalyst loading.

The performances of the MEAs with a catalyst loading of $0.4mg_{Pt/cm^2}$ (continuous lines) have higher performances compared to MEAs with $0.23mg_{Pt/cm^2}$ (dotted lines), for the two types of Pt salt (recycled and commercial) used for the catalyst synthesis. The impact of the catalyst loading on the cathode side is significant on the performances. The ECSA for the MEAs with high cathode catalyst loading ($0.4mg_{Pt/cm^2}$) are higher compared to the MEAs with low cathode catalyst loading ($0.23mg_{Pt/cm^2}$). The ratio of the ECSA between “high catalyst loading” and “low catalyst loading” are represented in the Figure 9-b). It seems that this ratio is in the same range than the ratio of the catalyst loading (represented in grey), that is coherent and explains (in part) the difference of performances.

Clean Hydrogen Partnership

Co-funded by the European Union

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

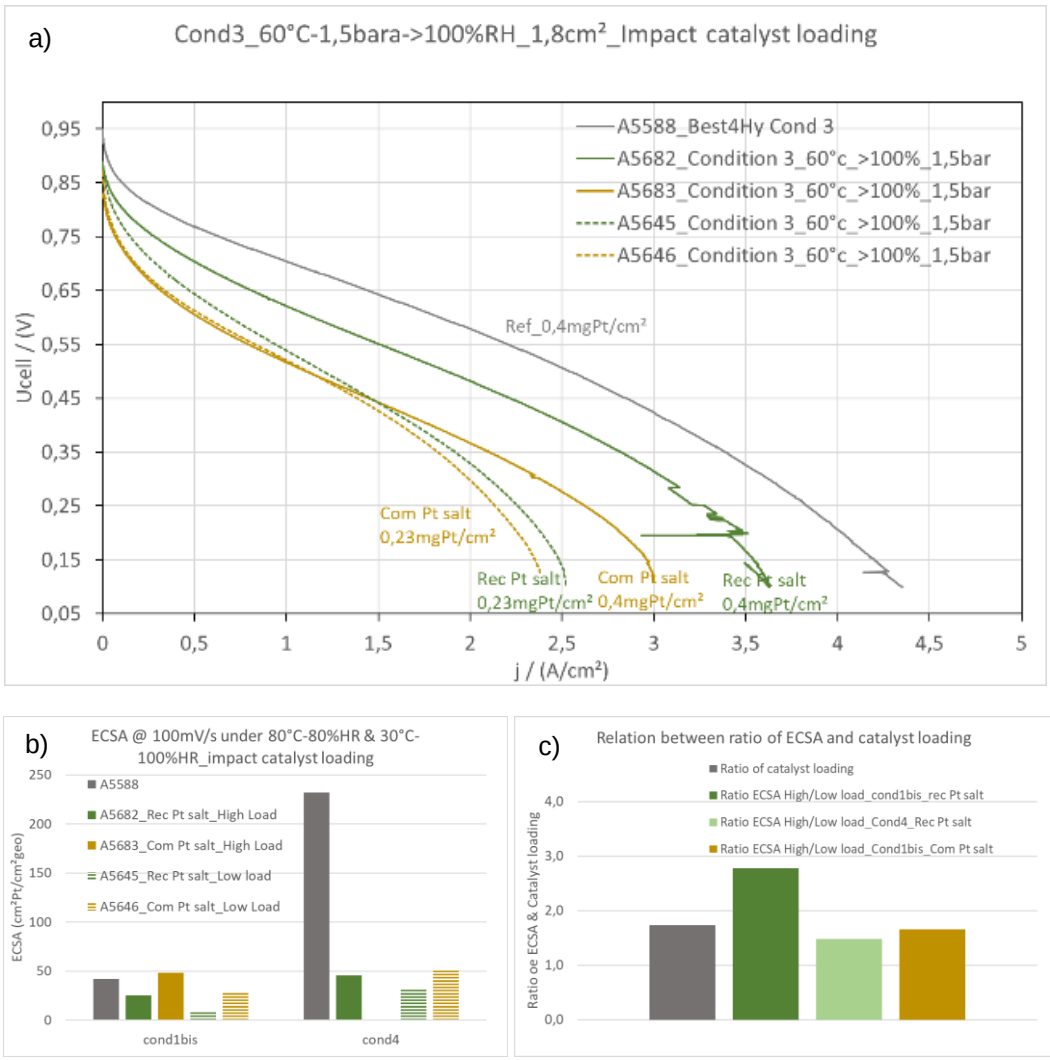


Figure 9: comparison of MEAs with different catalyst loading on the cathode side in 1.8cm² single cell a) polarization curves in cond3-60°C-1.5bara-100%RH; b) ECSA@100mV/s in cond1bis and cond4; c) relation between the ratio of the ECSA and the ratio of catalyst loading

The better performance with 'high catalyst loading" is also due to a better charge transfer in the electrodes (Figure 10 and Annex 4).

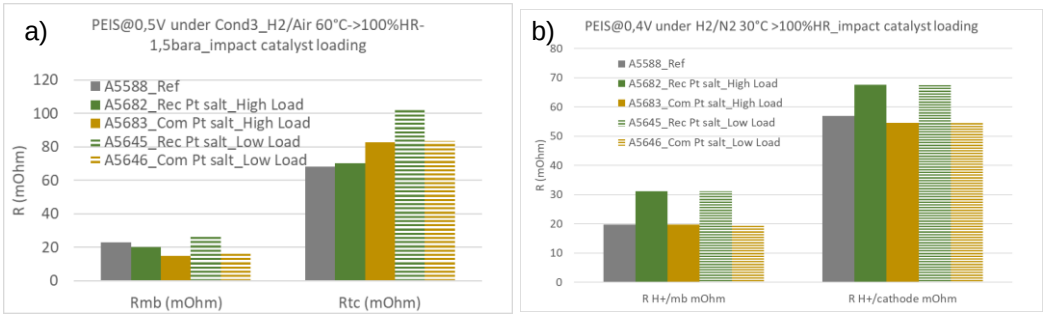


Figure 10 Comparison on the impact of the cathode catalyst loading at 0.23mg$_{Pt/cm^2}$ in dotted line and 0.4mg$_{Pt/cm^2}$ in continuous line, in 1.8cm² single cell, using catalyst synthesized with commercial Pt salt (A5646 & A5683) and recycled Pt salt (A5645 & A5682), compared to the reference MEA (A5588); a) PEIS@0.5V under H_2/air-cond3; and b) PEIS@0.4V under H_2/N_2-cond4

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

However, the performances of the MEA with recycled Pt salt (A5682) @ 0.4mg$_{Pt/cm^2}$ stay lower compared to the reference MEA (A5588), with a difference between 73% for condition 2 up to 88% of the performance in the condition 3, that corresponds respectively to a difference of 167mV and 84mV.

This observation leads to conclude that it might be necessary to optimize the ink formulation to improve the performances. However, it must be also highlighted that the process used for the MEA integrating the recycled catalyst is the spray (for these MEAs) whereas the one used for the reference MEA is the bar coater. The structure of the two electrodes can be different: the spray manufacturing can lead to a denser electrode at high loading. The bar coater process for the electrode manufacturing will be applied later as the up-scaled synthesis produces more than 1g of catalyst.

Thus, it was decided to use a loading on the **cathode side** of around **0.4mg$_{Pt/cm^2}$** for further testing. In these test conditions, in 1.8cm² single cell, we can say it is possible to use recycled Pt salt as precursor for the catalyst synthesis, without significant limitations of performances compared to the use of commercial Pt salt; but with a strong impact compared to a MEA manufactured with commercial components.

4.5 Impact of the Pt crystallites size

A batch of synthesized catalyst with the upscaled polyol reduction synthesis resulted in Pt crystallites size of 5nm, i.e. out of target (of 3-4nm). Catalyst with Pt crystallites size between 3 and 4nm are considered as optimized catalyst. It was considered interesting to evaluate its use so to maximise recycling of the recovered Pt.

This out of spec Pt was therefore evaluated on the anode side and on the cathode side independently to see the impact on the performance. This evaluation has been done in 1.8cm² and 25cm² single cell. The MEAs considered in this study are:

- The B4H reference MEAs (A5588_ref and A5605),
- The MEA with Pt of 5nm on the anode side (A5810),
- The MEAs with optimized crystallites Pt size on the cathode side (A5719 and A5718) and,
- The MEA with Pt of 5nm on the cathode side (A5809 and A5805),

which compositions are visible in the Table 6.

The performances in 1.8cm² and 25cm² single cell obtained vs the B4H reference MEA are represented in the Figure 11.

The performance of the MEA with Pt of 5nm on the anode side (A5810) is higher than the MEA with optimized recycled catalyst on the cathode side (A5719 & A5718) which is higher than the MEA with Pt of 5nm on the cathode side (A5809 & 5805). This trend is similar for the result in 1.8cm² or in 25cm² single cell.

Globally, we can say that we have:

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

- A decrease in performance using recycled catalyst with 5nm Pt on the anode side (A5810)
- A decrease in performance more pronounced (A5719 & A5718) using optimized recycled catalyst on the cathode side,
- A decrease in performance more pronounced again (A5809 & 5805) using recycled catalyst 5nm Pt on the cathode side,
- A decrease in performance with 5nm Pt crystallites size on the cathode side (A5809 & 5805) compared to the optimized size of the recycled catalyst (A5719 & A5718) on the cathode side.

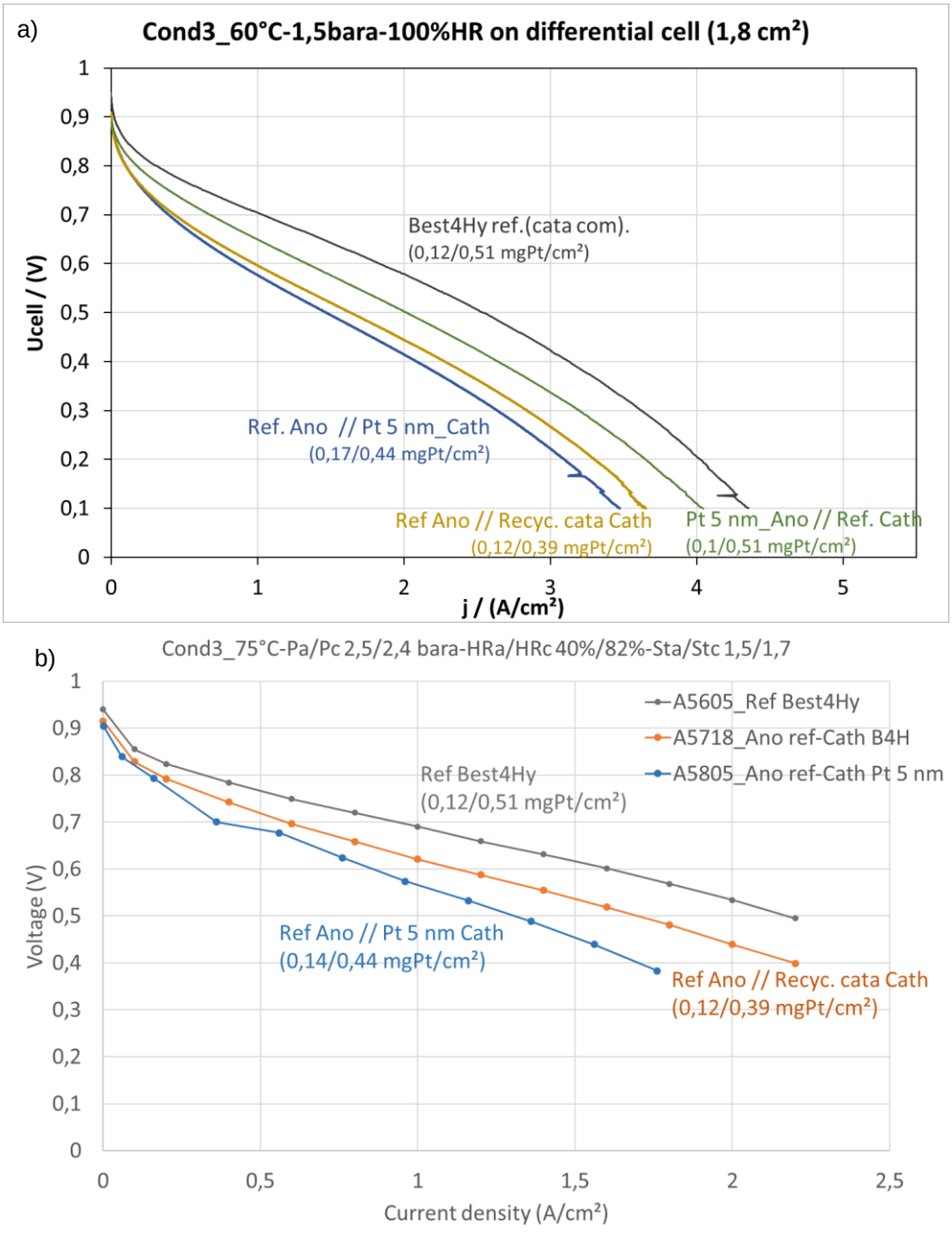


Figure 11 impact of the 5nm Pt crystallites size on the performances a) in 1.8cm² single cell; b)in 25cm² single cell

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical analyses in 1.8cm²:

In 1.8cm² single cell, the difference in performance can be explained by the lower active area on the cathode side, compared to the reference MEA. The loss in active area with recycled catalyst with 5nm Pt crystallites size on the cathode side (blue histogram on the Figure 12-a) is around 66% compared to the B4H reference MEA, whereas the loss in performance is only of 43% with the optimized recycled catalyst. The low performance of the MEA with 5nm Pt crystallites size on the cathode side is linked to the low ECSA, a high protonic resistance in the cathode and a high charge transfer resistance in the electrode. No significant impact is noticed on the ECSA when the 5nm Pt crystallites are on the anode because the cathode is made in this case with commercial catalyst. However, the non-optimized catalyst on the anode causes around 7% loss of performance (in size 1.8cm²) compared to the B4H reference MEA, and 18% when this catalyst is on the cathode side (observations done in Cond3); the protonic resistance in the cathode being lower compared to the reference MEA.

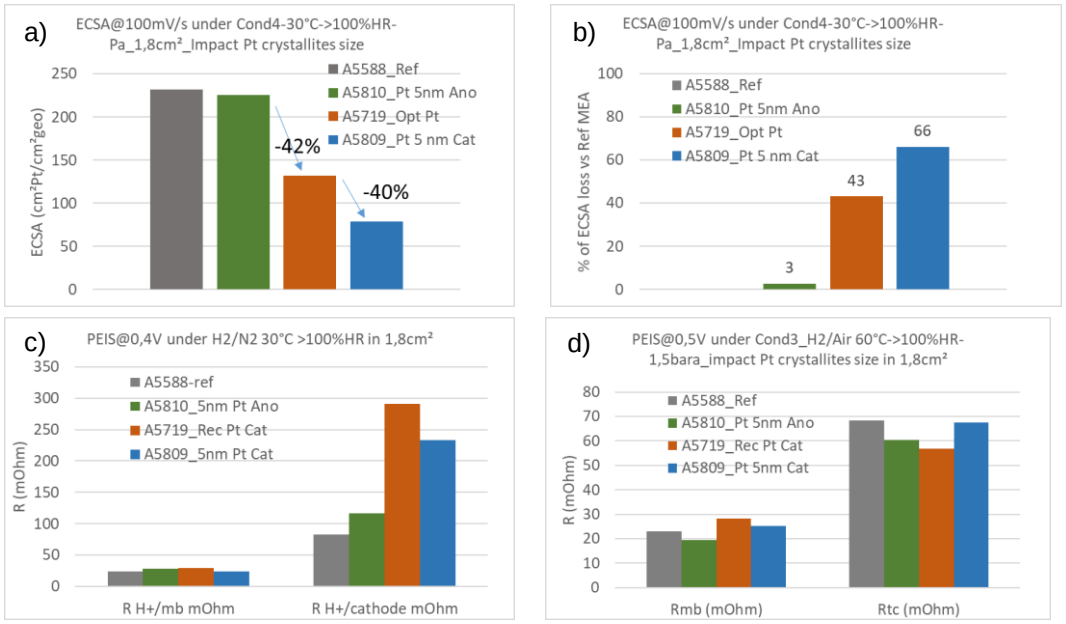


Figure 12: electrochemical characterization in 1.8cm² of MEA including catalyst with 5nm Pt crystallites size; a) ECSA; b) % of loss of ECSA vs reference MEA; c) PEIS@0.4V under H2/N2 30°C-Pa->100%RH and d) PEIS@0.5V under H2/air 60°C-1.5bara->100%RH

This means that a non-optimized catalyst on the anode side can affect the global performance of the MEA, but less than if the non-optimized catalyst is on the cathode side.

Electrochemical analyses in 25cm²:

The Figure 13 represents the result of electrochemical characterization done in size 25cm². The % of loss of ECSA is calculated for the different MEAs. The values of the % of loss of ECSA in 1.8cm² and in 25cm² sizes are similar.

There is a loss of 29% of ECSA when using 5nm Pt crystallite size on the cathode side (A5805) compared to an optimized catalyst with between 3 and 4nm Pt size (A5718), corresponding to a loss of 64% compared to the reference. There is a loss of 53% of ECSA

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

when using recycled catalyst with optimized Pt crystallites (between 3 and 4nm) compared to the reference MEA, corresponding to a decrease of 10% in performance in condition 3. The low ECSA with 5nm Pt crystallite size on the cathode side is linked to a high protonic resistance in the cathode (Figure 13), probably due to a bad contact between the ionomer and the Pt of the catalyst that is a little agglomerate on the carbon support.

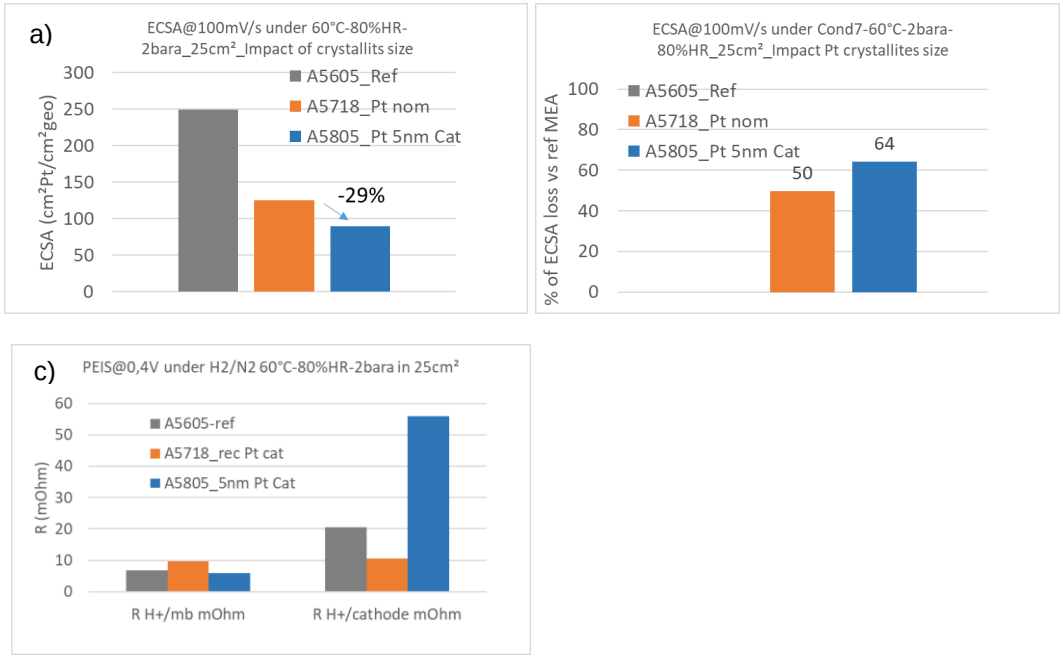


Figure 13: electrochemical characterization in 25cm² of MEA including catalyst with 5nm Pt crystallites size under 60°C—2bara-80%RH; a) ECSA; b) % of loss of ECSA vs reference MEA and c) PEIS@0.4V

The % of the performance vs the reference MEA represented in Figure 14 highlight that the MEA including optimized recycled catalyst (A5718) reaches performances of more than 87% whatever the conditions. This corresponds to a difference of 130mV @ 1A/cm² in the condition 3. Taking into account the previous observations of the impact of the recycled catalyst on the anode side, we can expect that the performance in 25cm² could be really close to the reference MEA, at least more than 87%.

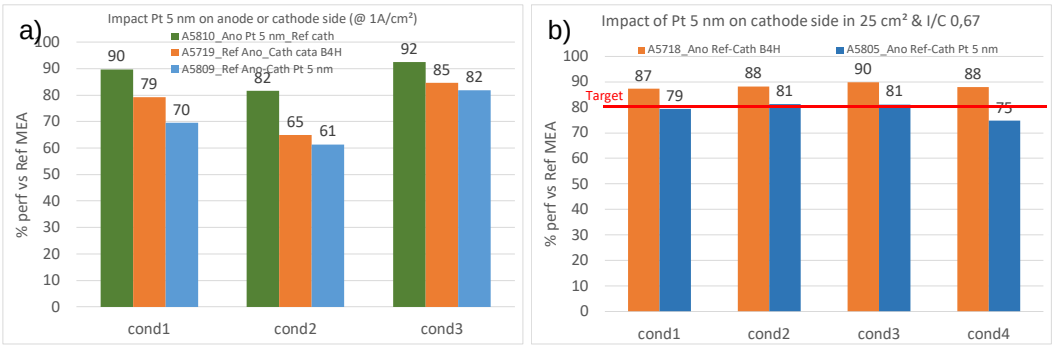


Figure 14 impact of the 5nm Pt crystallites size on the % of performance vs B4H Reference MEA in a) 1.8cm² single cell; b) in 25cm² single cell

Between the two types of single cell, 1.8 and 25cm², we have similar value in term of loss of performance when the recycled catalyst is put on the cathode side. The impact on the

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

performance with 5nm Pt catalyst on the anode side is less important compared to the same catalyst put on the cathode side.

In conclusion, if necessary, the catalyst with **5nm Pt crystallites size** could be introduced on the **anode side** for the manufacturing of the large CCM, if the quantity of the optimized catalyst not be sufficient. This also means that larger quantities of catalyst with recycled Pt can be used in a closed loop.

In this study, some interesting results have been obtained using recycled catalyst, independently on the anode side and the cathode side; but the performance of the MEAs are still lower compared to the B4H reference MEA when it is introduced on the cathode side. A way to increase the performance is to modify the ink formulation, like adapting the ratio of the ionomer on carbon (I/C). An objective is to manufacture MEA with at least more than 90% of recycled catalyst.

4.6 Impact of the I/C ratio

To increase the performance of MEA with recycled catalyst, it was chosen to study the ratio of the ionomer onto the carbon (I/C) in the ink formulation, varying it between 0.57 and 0.87.

The MEAs and their I/C ratio, considered in this study are:

- The B4H reference MEA (A5588 and A5605)
- MEAs with I/C=0.57 (A5712 and A5711)
- MEAs with I/C=0.67 (A5719 and A5718)
- MEA with I/C=0.77 (A5811)
- MEAs with I/C=0.87 (A5812 and A5808)

These MEAs, which the compositions are visible in theTable 6, have been tested in 1.8cm² and 25cm² single cell.

The polarization curves (Figure 15**Erreur ! Source du renvoi introuvable.**) show the following escalation of performance of the MEAs, in 1.8cm² and 25cm² single cell:
with I/C 0,67 < I/C 0,77 < I/C 0,57 = I/C 0,87 < B4H Ref MEA.

Globally, the performance increases with the increase of the I/C ratio. It is important to notice that the MEAs with the ratio I/C 0.77 and 0.87 have recycled catalyst on both sides, whereas MEAs with ratio I/C 0.57 and 0.67 have recycled catalyst on the cathode side only. This difference can explain why the performance of the MEA with I/C 0.57 is the same of the MEA with I/C 0.87; the anode of the MEA with I/C 0.57 has commercial catalyst; the ECSA, visible in the Figure 16-a, are also similar, in 1.8cm² single cell.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

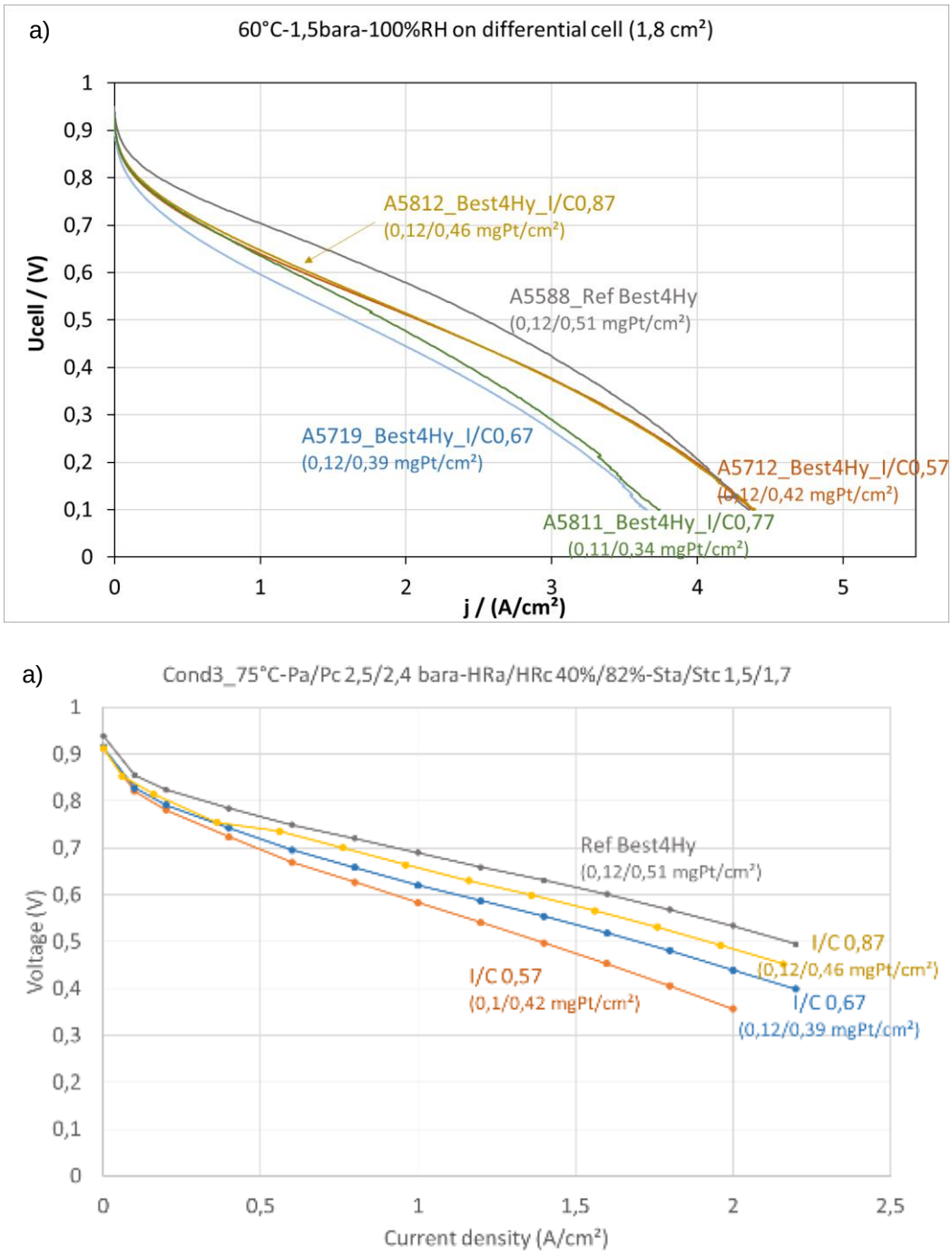


Figure 15 impact of the I/C ratio in the ink formulation of MEAs in term of performances in a) 1.8cm² single cell; b) 25cm² single cell

Considering the other conditions (cond1, cond2 and cond4, visible in the Annex 6), MEA with I/C 0,87 with recycled catalyst on both sides, seem to have the performance closest to the B4H reference MEA.

The electrochemical characterization (Figure 16) shows that the protonic resistance in the cathode and the charge transfer of the MEA with I/C 0.87, in 1.8cm² size, is the lowest compared to the others; and the ECSA of this MEA is the highest with a loss of 36% of ECSA vs the B4H reference MEA. This loss of ECSA can reach up to 59% vs the B4H reference MEA with a non optimized ink formulation.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

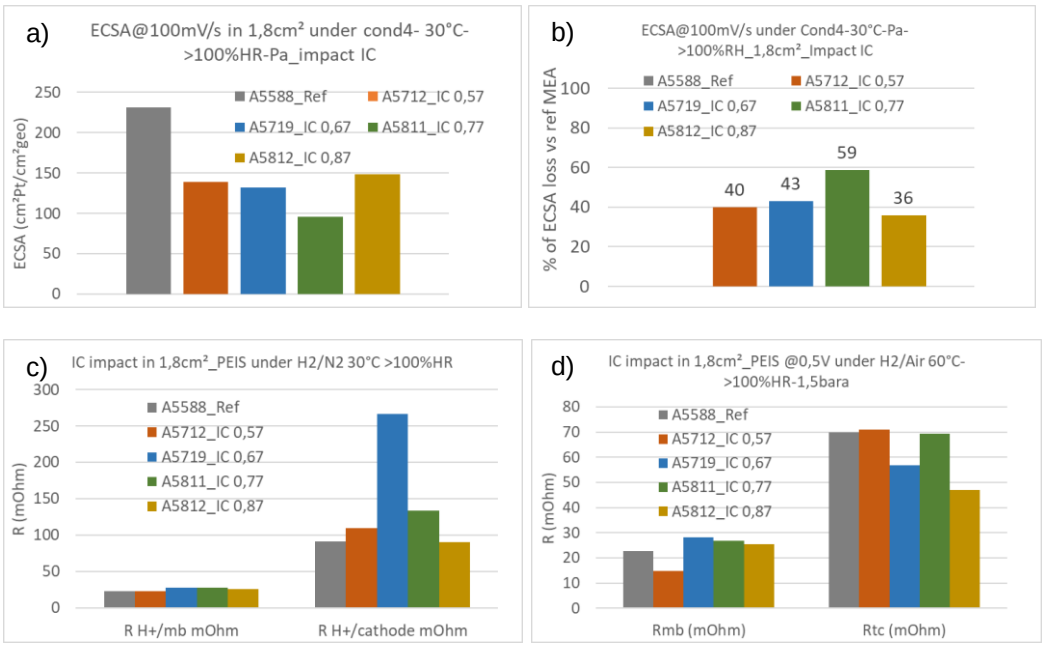


Figure 16: electrochemical characterization in 1.8cm² of MEAs with different I/C ratio;
a) ECSA@100mV/s under H_2/N_2 30°C-Pa->100%RH;
b) % of loss of ECSA vs B4H reference MEA;
c) PEIS@0.4V under H_2/N_2 -30°C->100%HR-Pa;
d) PEIS@0.5V under H_2/Air-60°C-15bara->100%RH

In 25cm² single cell (Figure 17), the loss of ECSA of the MEA with the ratio of I/C=0.87 is also the lower compared to the B4H reference MEA, the protonic resistance in the membrane of this MEA being the lowest.

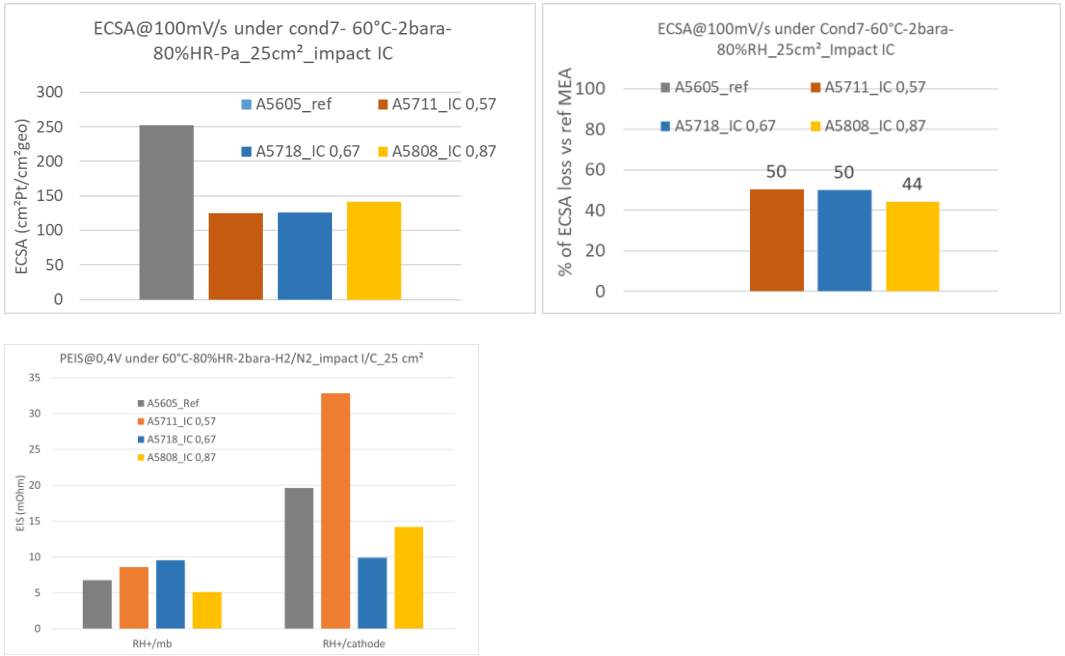


Figure 17: electrochemical characterization in 25cm² of MEAs with different I/C ratio under 60°C-15bara->100%RH; a) ECSA; b) % of loss of ECSA vs reference MEA; c) PEIS@0.4V under H_2/N_2

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Concerning the ECSA, the trend of the loss in active surface area is really similar between 1.8cm² and 25cm² single cell. The ECSA is globally divided by 2 between the MEAs with recycled materials and the B4H reference MEA. Globally, the MEA with I/C 0.87 has a good protonic conductivity in the membrane and in the cathode, and this is not limited by the charge transfer in the electrode, compared to the others MEAs with different I/C ratio; even if the electrochemical surface area of the cathode is divided by 2 compared to the B4H reference MEA.

The % of performance calculated in Figure 18 show that this % of performance (calculated vs B4Hy reference MEA) increases with the increase of the I/C ratio. Finally, **Erreur ! Source du renvoi introuvable.**the MEA with I/C 0.87 can reach around **96%** in an EKPO condition (cond3) of performance in 25cm² single cell compared to the B4H reference MEA; that corresponds to 30 mV difference. More generally, more than 91% of performance is reached compared to the reference MEA, with I/C 0,87 and recycled catalyst on both side (anode and cathode).

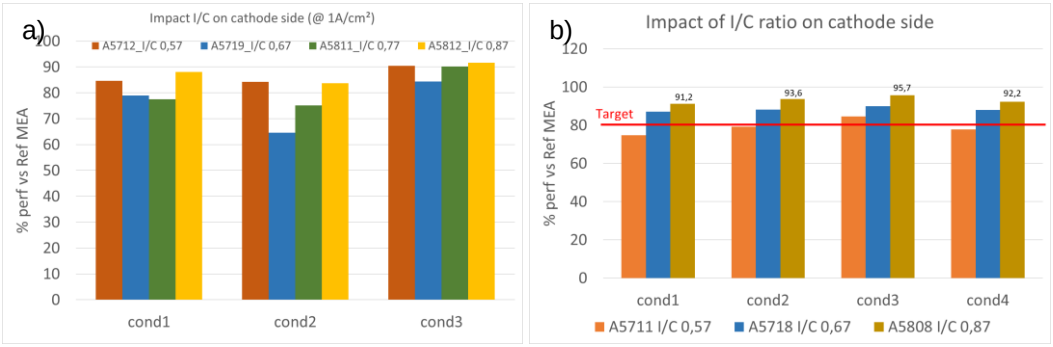


Figure 18 impact of the I/C ratio in the ink formulation of the % of performance vs B4H Reference MEA in a) 1.8cm² single cell; b) 25cm² single cell

➔ All these results allows to conclude that a composition of the inks with a ratio of **I/C 0.87 with recycled catalyst on both side, anode and cathode side**, can reach the target of the project, in term of performance.

4.7 Comparison of performance between MEA with the optimized ink composition vs EKPO MEA

As the composition of the MEA is selected, a comparison can be done between the MEA with the optimized ink composition vs the B4H reference MEA and the EKPO MEA. The MEAs considered in this study are:

- EKPO MEA A5526,
- The B4H reference MEA A5605 and,
- MEA including optimized ink composition with recycled catalyst A5808,

Which the compositions are visible Table 6.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

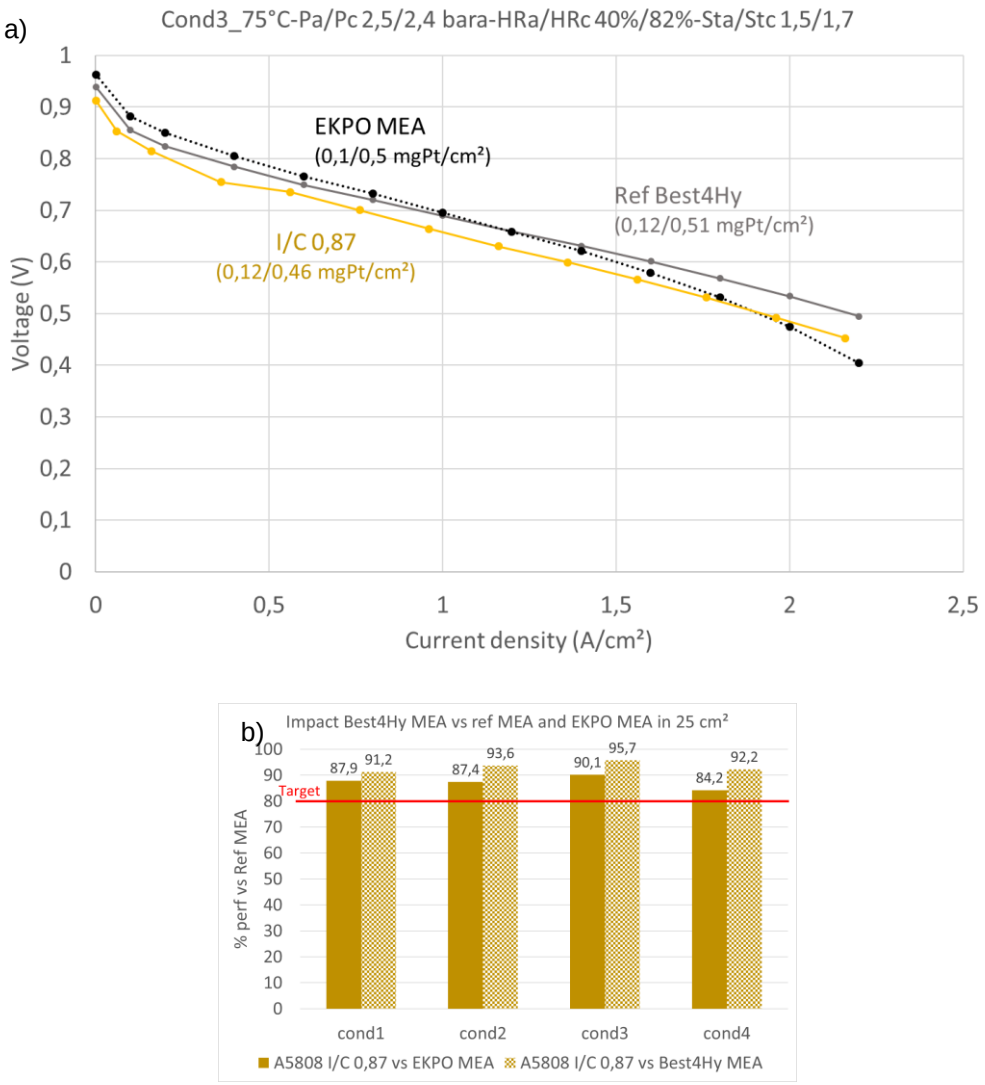


Figure 19 Comparison of MEAs with an optimized ink composition including 100% of recycled catalyst vs B4H reference MEA and EKPO MEA a) polarization curve ; b) % performance of MEA

The polarization curves show that the performance of the B4H reference MEA is slightly lower than the EKPO MEA up to 1A/cm² in an EKPO condition; after this current density, the performance becomes higher. The MEA including recycled catalyst with an optimized ink formulation has lower performance compared to the reference MEA and EKPO MEA.

Compared to the B4H reference MEA, the MEA including recycled catalyst with an optimized ink formulation (A5808) with I/C=0.87 reaches:

- **96%** of performance in an EKPO condition; that corresponds to 30 mV difference
- More generally, more than 90% of performance reached with an optimized ink composition integrating 100% of recycled catalyst compared to B4H reference MEA

Compared to the EKPO MEA, the MEA including recycled catalyst reaches:

- **90%** of performance in an EKPO condition; that corresponds to 35 mV difference
- More generally more than 84% of performance reached with an optimized ink composition integrating 100% of recycled catalyst compared to EKPO MEA

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

In conclusion, **96%** of performance @ **1A/cm²** vs B4H reference MEA in **25 cm²** in condition 3 (EKPO 75°C-Pa 2,5b-Pc2,4b-HRa 40%-HRc 82%-Sta 1,5-Stc 1,7) has been reached with an ink composition with a ratio of **I/C 0,87**, with **100% of recycled catalyst** (anode & cathode side).

➔ *This confirms the **selection of I/C 0,87 including recycled catalyst on both sides (anode and cathode), for manufacturing large CCMs.** This corresponds to the **MS5 Selection of MEA composition including recycled materials for large scale CCM manufacturing.***

Conclusions

5

This document presented the performances obtained in single cell of MEA manufactured with recycled components, in our case, the catalyst. Different studies including the recycled catalyst in the MEAs permitted to conclude that:

- The BEST4Hy reference MEA has performances close to the EKPO MEA with a positive impact from 1.2A/cm² (0.69V@1A/cm² for the reference MEA vs 0.73V for EKPO MEA)
- It's possible to use recycled Pt salt for the catalyst synthesis without affecting the performance vs the use of commercial Pt salt
- The cathode catalyst loading has significant impact on the performances, an amount of 0.4mg$_{Pt/cm^2}$ is preferable compared to 0.23mg$_{Pt/cm^2}$
- Catalyst with 5nm Pt crystallites size can be used on the anode side with only 13% loss of performances compared to the reference MEA
- The optimized ratio of Ionomer/Carbon in the recycled catalyst is I/C=0.87
- It is possible to use recycled catalyst on both sides, on the anode and on the cathode side, and to recover up to 96% of performance compared to the B4H reference MEA in a specific condition.

A composition of electrodes has been selected for MEAs to reach the target of the project in term of performances. Some **96%** of performance @ **1A/cm²** vs BEST4Hy reference MEA in **25 cm² cells in a condition coming from stack operation** (cond3_EKPO 75°C-Pa 2,5b-Pc2,4b-HRa 40%-HRc 82%-Sta 1,5-Stc 1,7) has been reached with an ink composition with a ratio of **I/C 0,87, with 100% of recycled catalyst (anode & cathode side)**. This selection is linked *to the **MS5 Selection of MEA composition including recycled materials for large scale CCM manufacturing.***

The next step is to manufacture 10 CCM to EKPO stack design with the selected ink formulation. These CCM will be evaluated in a short stack using a test protocol defined between EKPO and CEA.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Annexes

Annex 1: electrochemical characterization

Some electrochemical characterizations are presented and used to analyse the difference in term of performance of the MEAs tested.

The electrochemical impedance spectrum (EIS) obtained in hydrogen-air and hydrogen-nitrogen are respectively represented in the figures below.

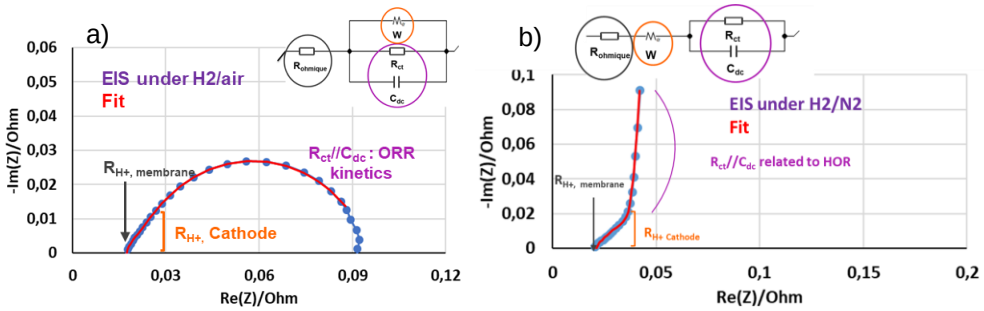


Figure 20: example of electrochemical impedance spectrum and their equivalent circuit obtained in a) H2/air and b) in H2/N2

These equivalents circuits are used to fit the spectrum and to calculate:

- The membrane resistance (R_{mb}) and the charge transfer resistance (R_{tc}) for EIS done in H_2/air
- The protonic resistance in the membrane ($R_{H+/mb}$) and the protonic resistance in the working electrode, the cathode ($R_{H+/cathode}$) for EIS done in H_2/N_2

The cyclic voltammetry (VC) that is a sweep in voltage between a minimum and a maximum value allows to calculate the electrochemical surface area (ECSA) that corresponds to the hatched zone in the Figure 21. The expression used to calculate this area is:

$$S_{Pt} = \frac{Q_{H/Pt}}{\mu_{H/Pt}}$$

Where S_{Pt}: the ECSA, the electrochemical surface area (cm^2_{Pt}/cm^2_{geo});
$Q_{H/Pt}$: proton adsorption on the Pt (µC);
$\mu_{H.Pt}$: specific charge of the Pt for the hydrogen adsorption = 210µC.cm^{-2}

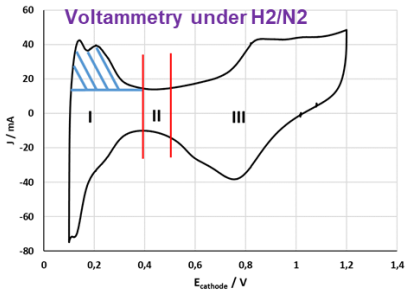
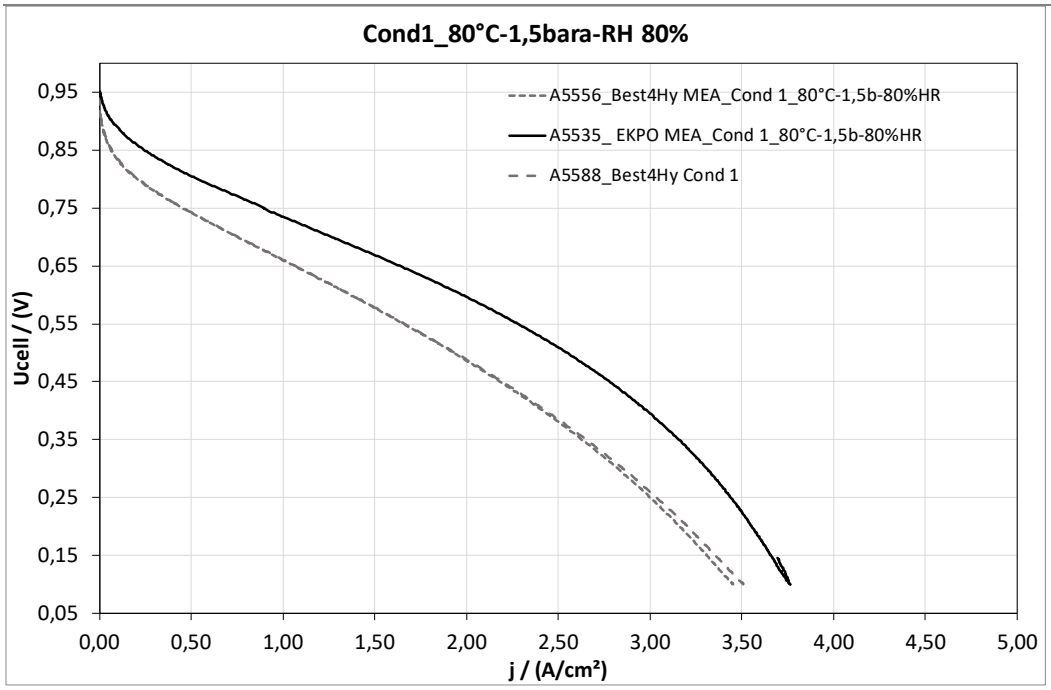


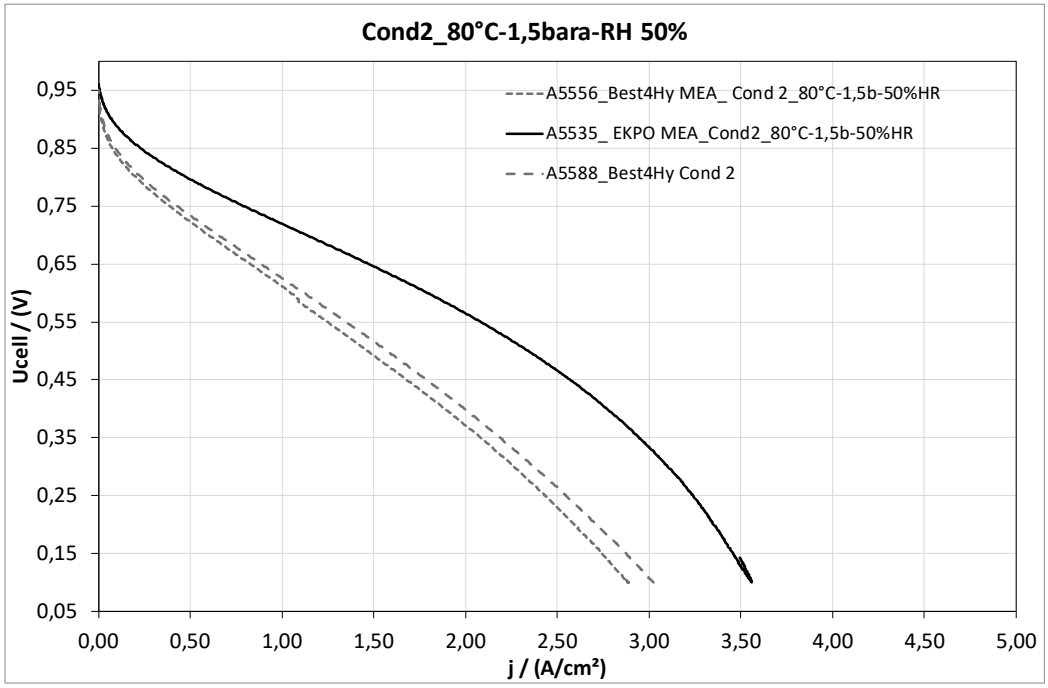
Figure 21: example of cyclic voltammetry

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

In 1.8cm²

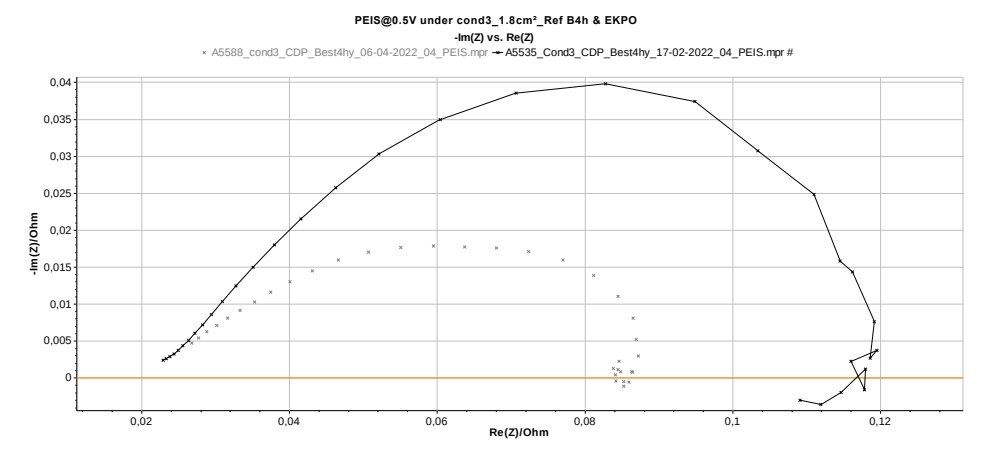
Polarization curves

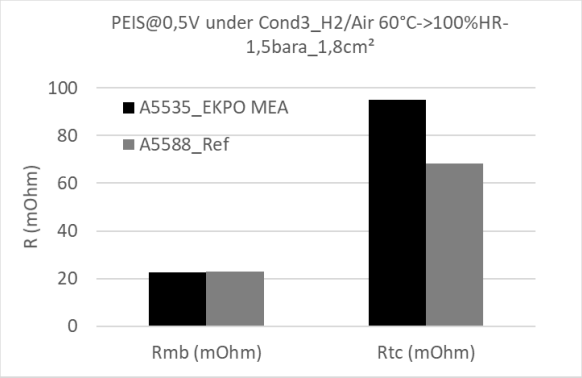




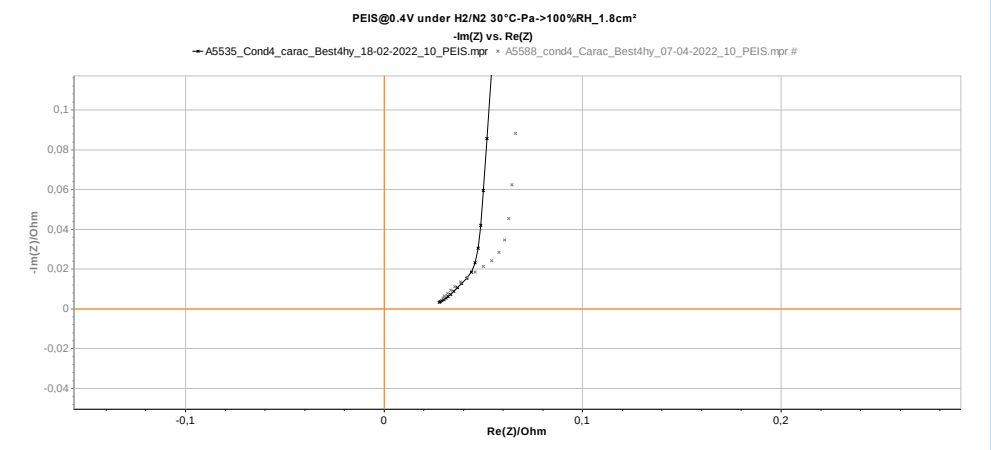
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

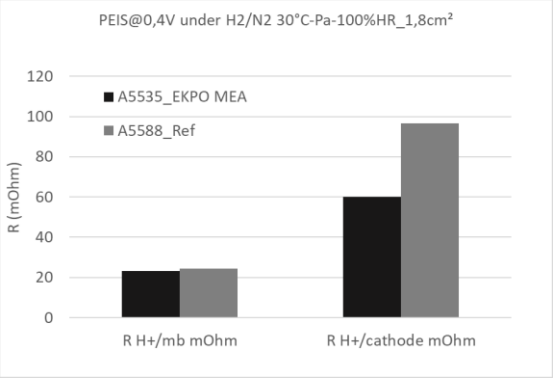
Electrochemical characterization under Cond3-H2/Air-60°C-1.5bara->100%RH:



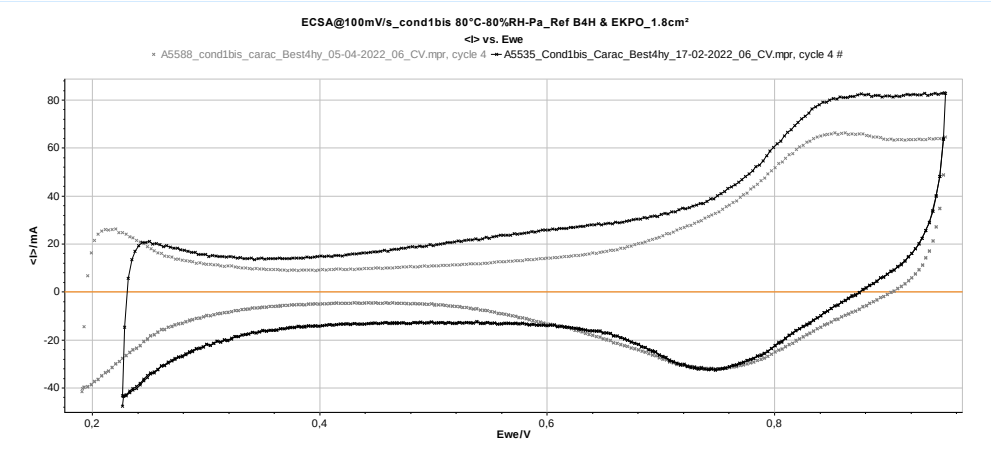


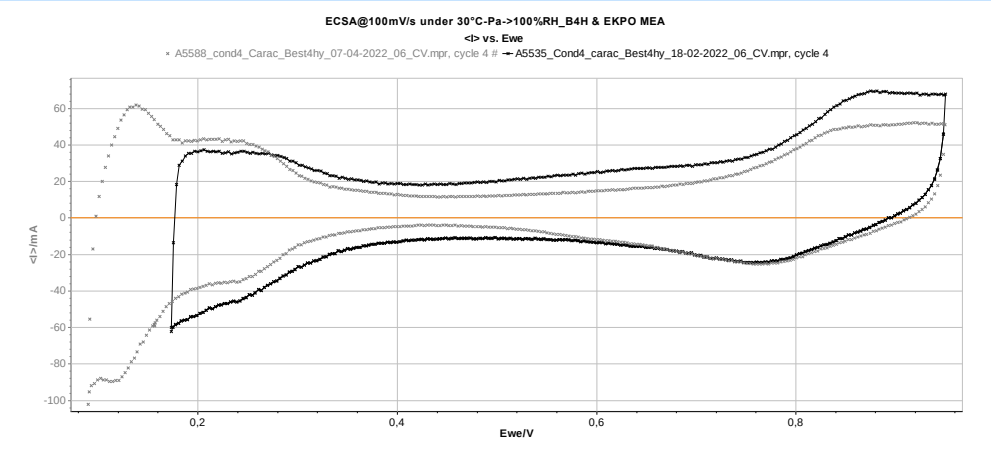
Electrochemical characterization under Cond4-H2/N2-30°C-Pa->100%RH:

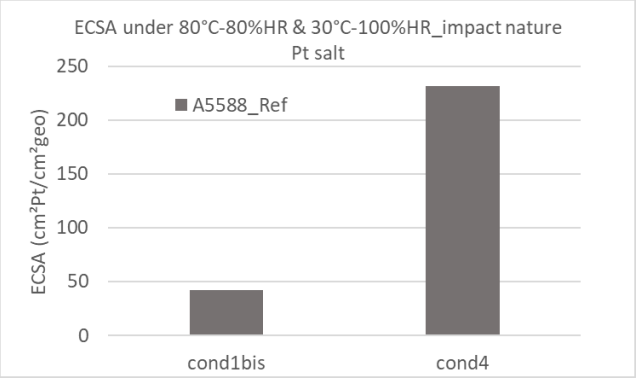




This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.





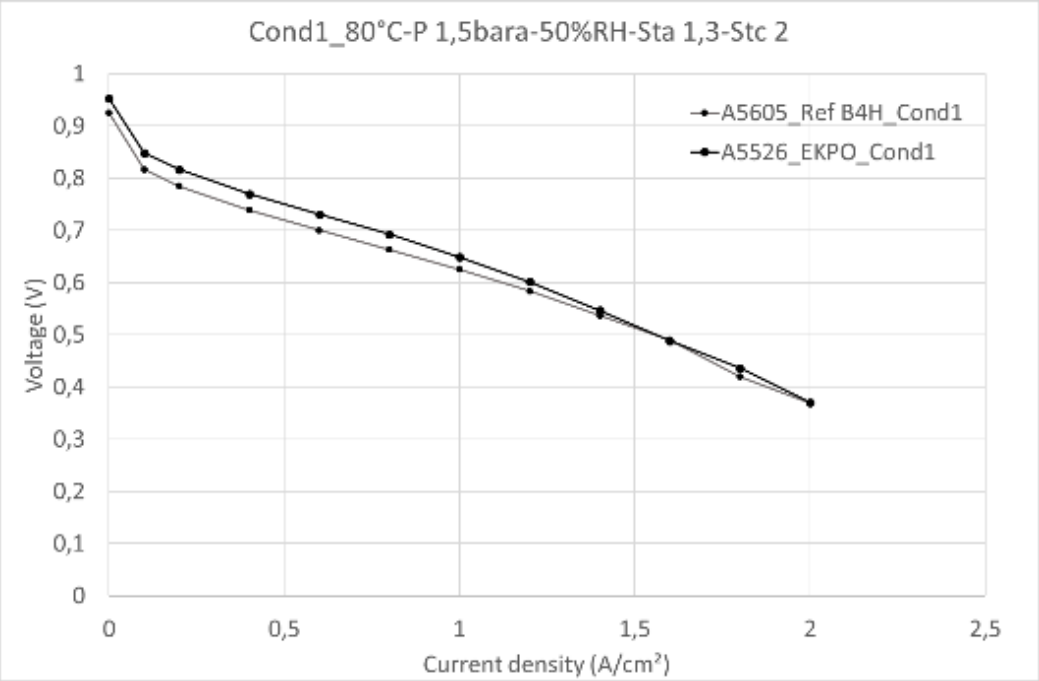


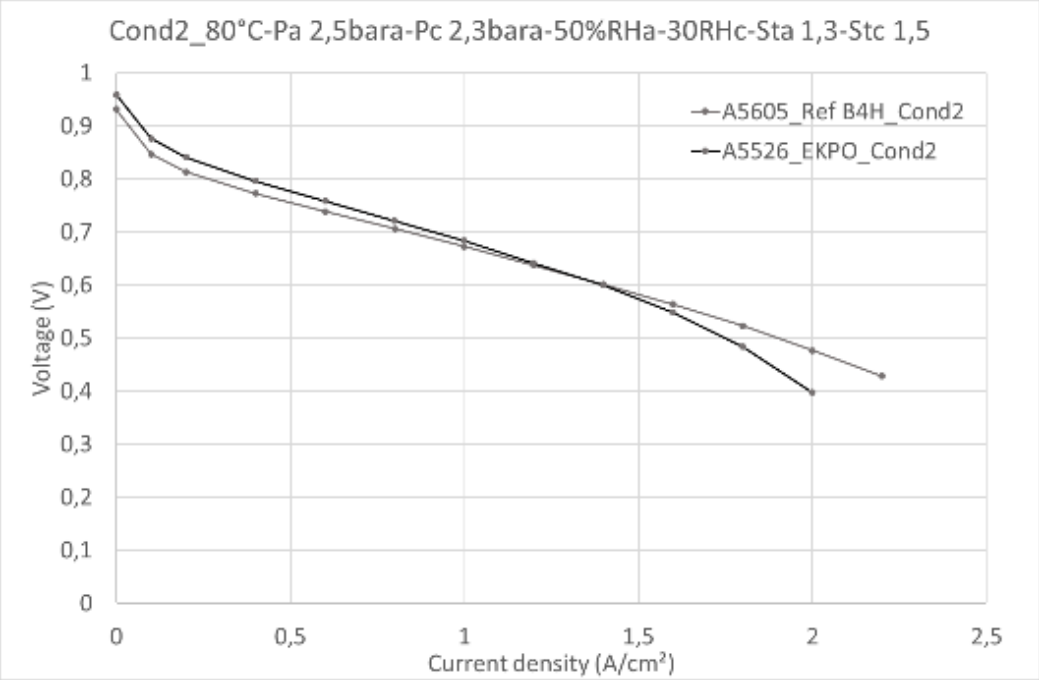
The ECSA has been calculated from the curves obtained with the cyclic voltammetry (CV) experiment. The calculation of the ECSA (in cm^2_{Pt}/cm^2_{geo}) uses the specific charge of the Pt for the hydrogen adsorption of 210µC.cm^{-2}. However, the catalyst used in the EKPO MEA is a bi-metallic catalyst, i.e Pt + other metal deposited on Carbon. After a research in the literature, no specific value exists for this type of catalyst; the value commonly used is 210µC.cm^{-2}. Thus, the calculated values for the EKPO MEA give an idea about the active surface area. Moreover, for EKPO MEA, the experiment of the CV has not been realized in the same condition (due to a problem during the test) as the B4H reference MEA (curves presented in Annex 2). The minimum limit potential (Ei mV) for the potential ramp for the CV is not the same, leading to make a wrong comparison with B4H reference MEA, because the area of the integration is not the same. This explains why the comparison of the ECSA between the MEAs are not possible.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

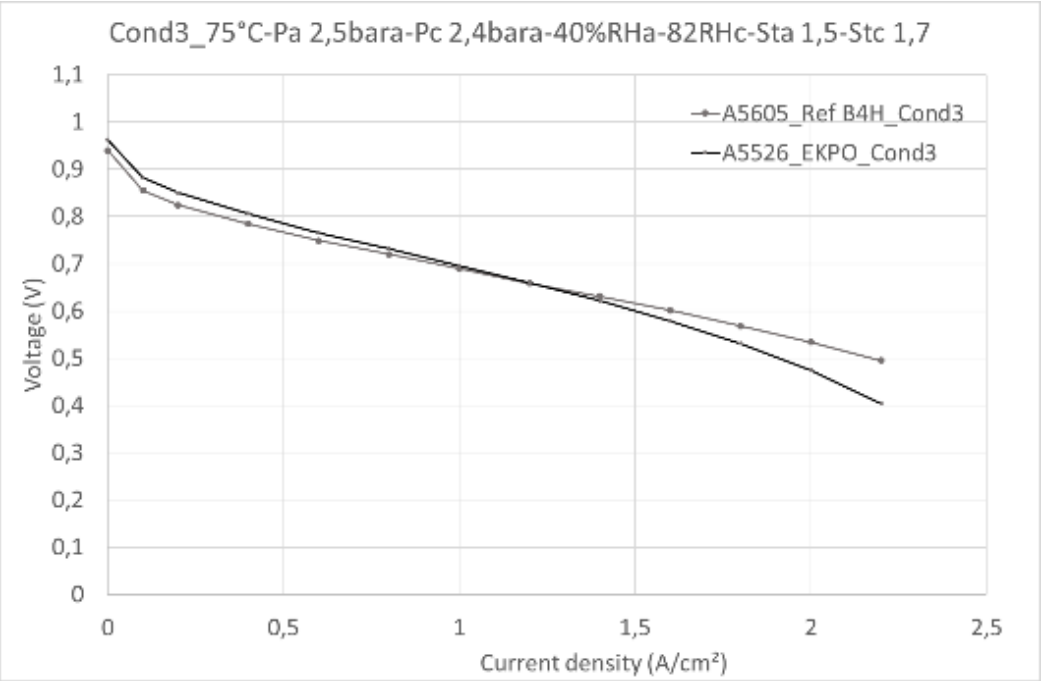
In 25cm²

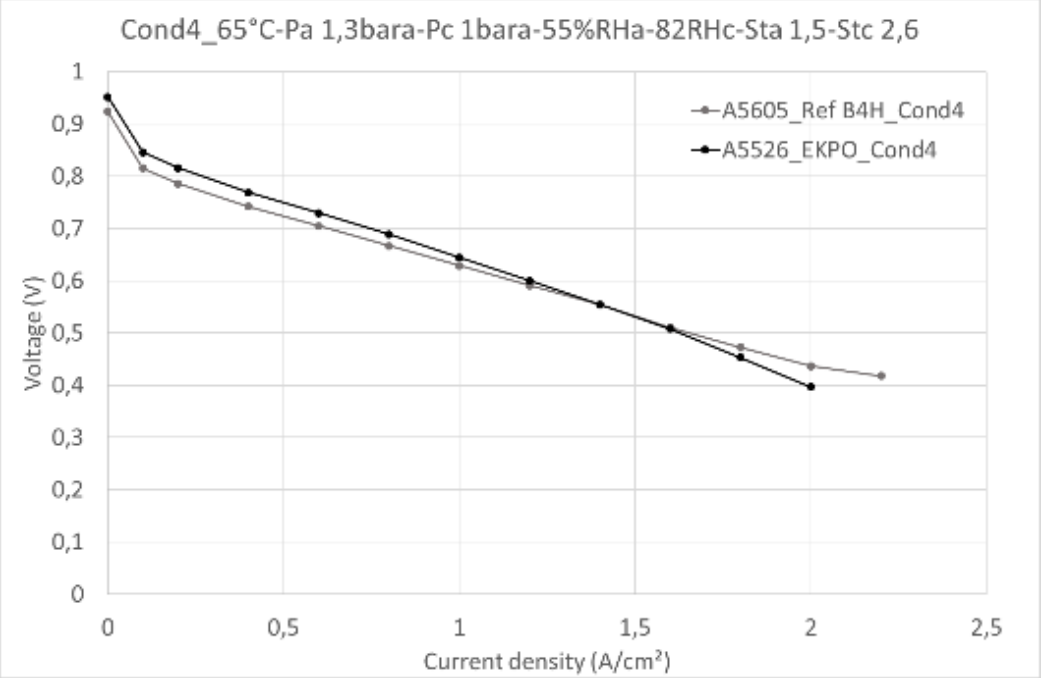
Polarizations curves





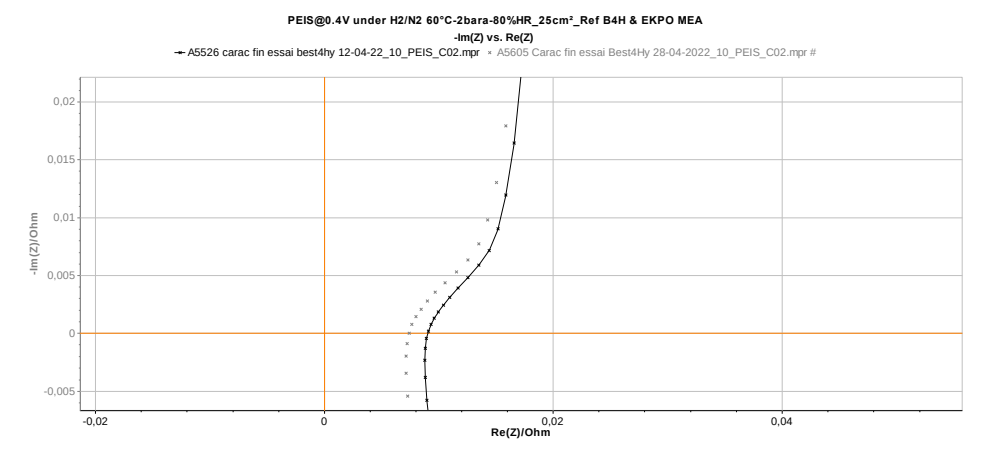
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

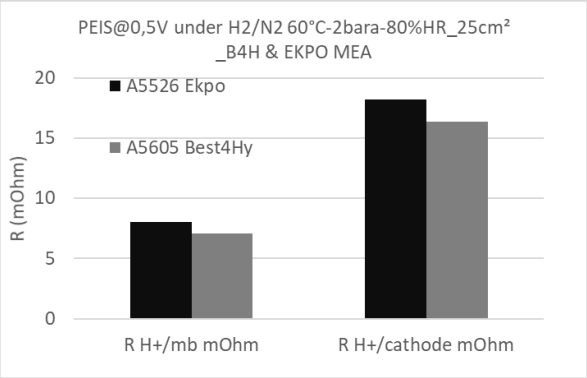


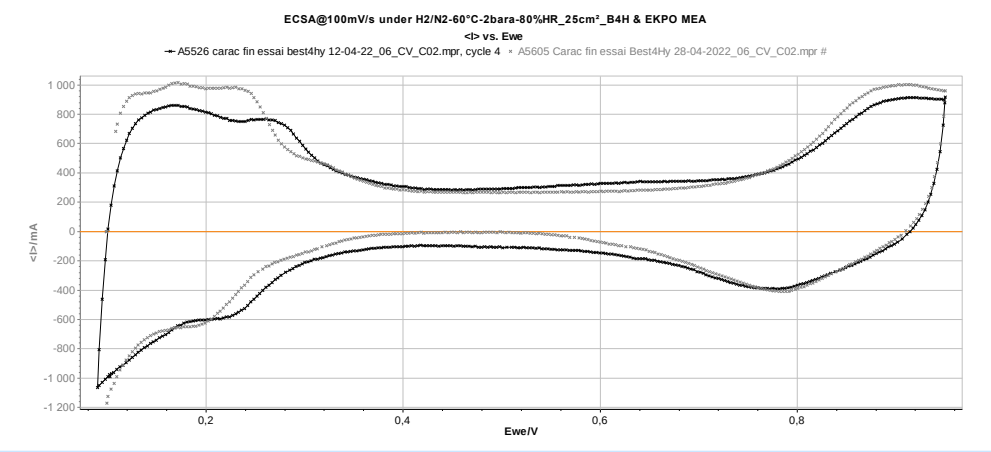


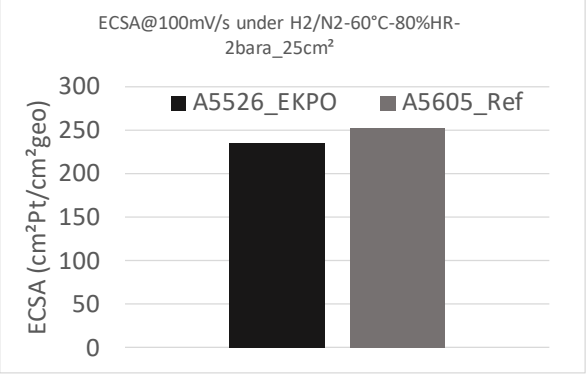
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under Cond7-H2/N2-60°C-2bara-80%RH









The calculation of the ECSA of EKPO MEA is just an estimation. Indeed, as the catalyst used for EKPO MEA is a bimetallic catalyst, using the value of 210µC.cm^{-2} for the calculation is not correct, but can give an idea about the ECSA.

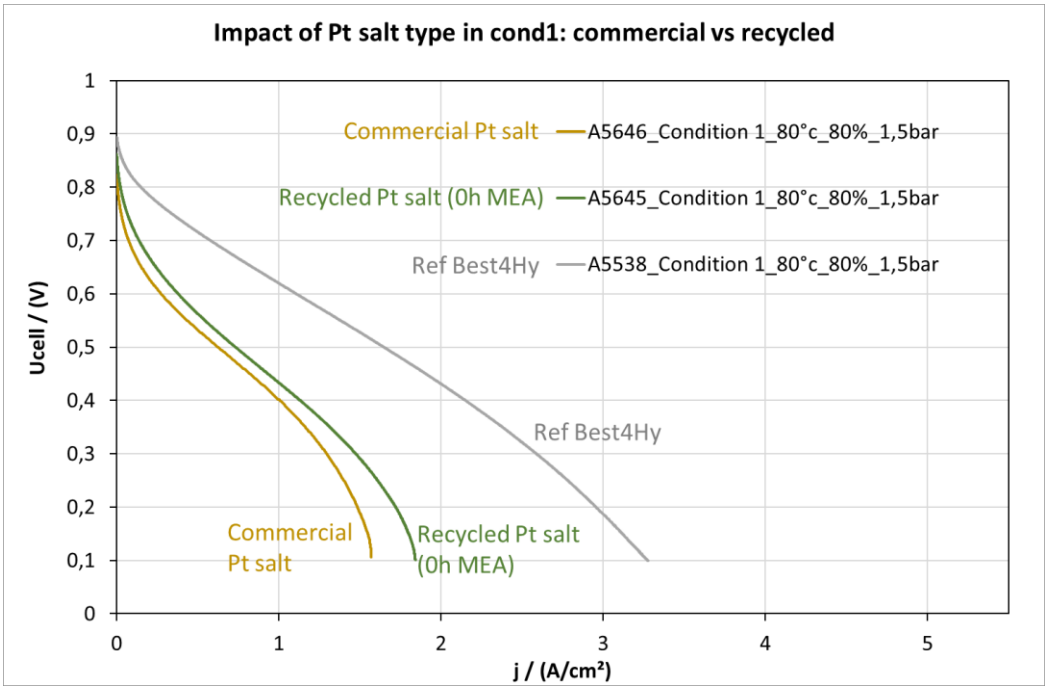
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

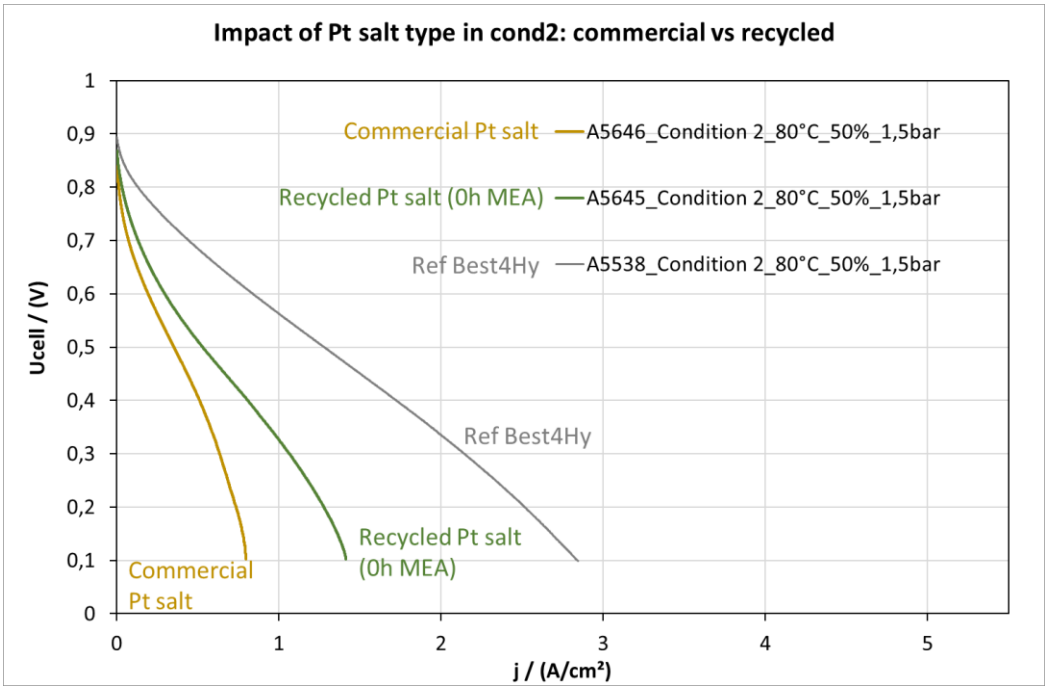
Annex 3: impact of the type of Pt salt: commercial vs recycled

These tests are done only on 1.8cm² size cells and with low catalyst loading of 0.23mgPt/cm².

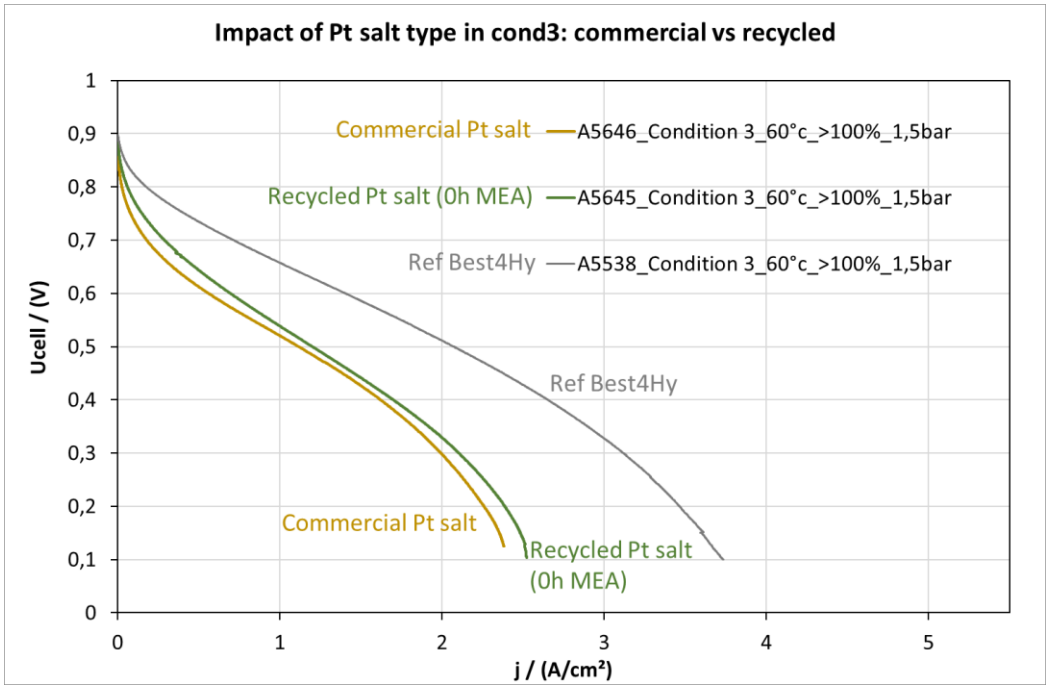
1.8cm² & 0.23mgPt/cm² on the cathode side

Polarizations curves

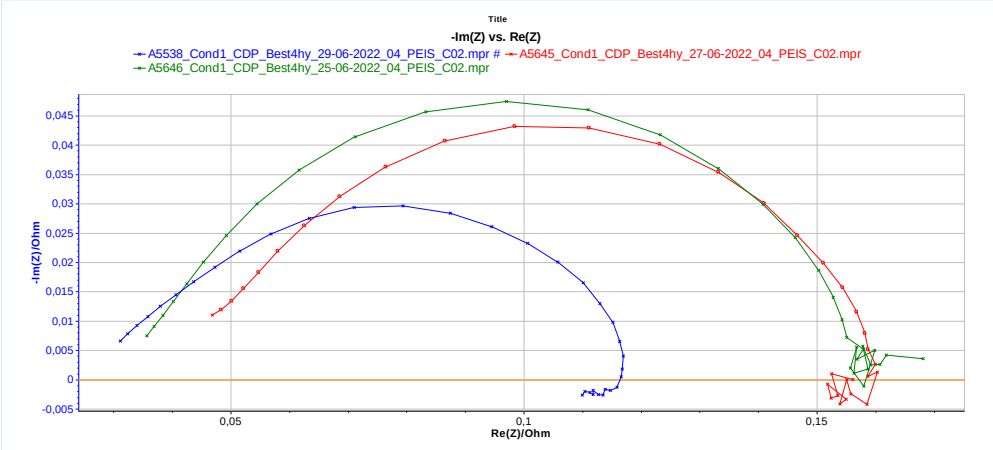


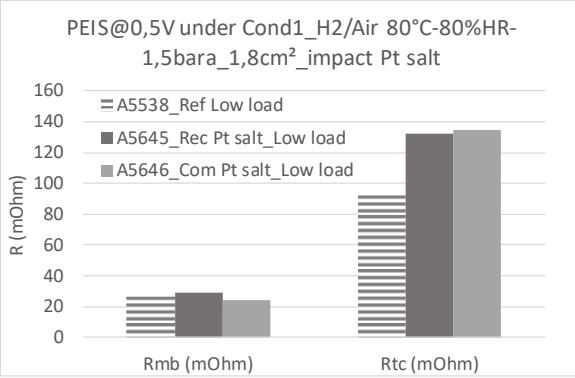


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



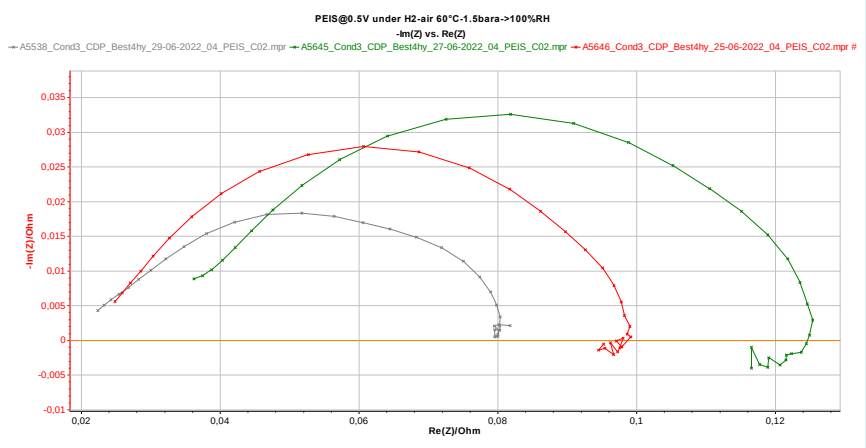
Electrochemical characterization under Cond1-H2/Air-80°C-1.5bara-80%RH

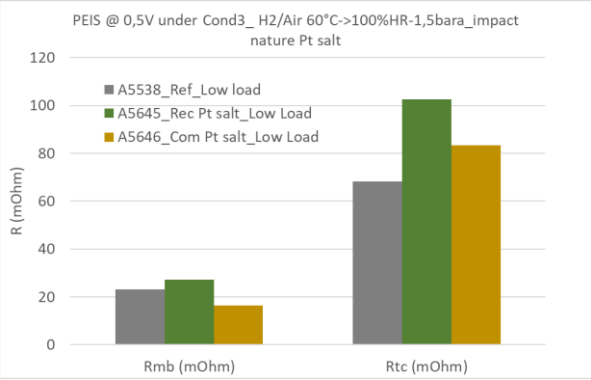




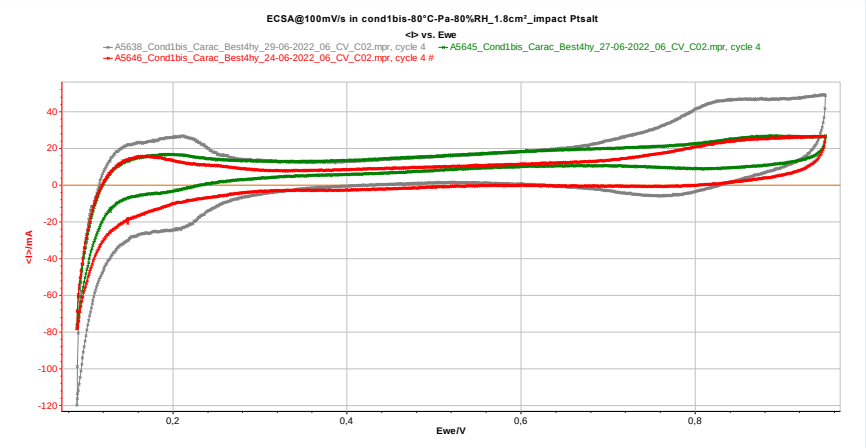
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under Cond3-H2/Air-60°C-1.5bara->100%RH

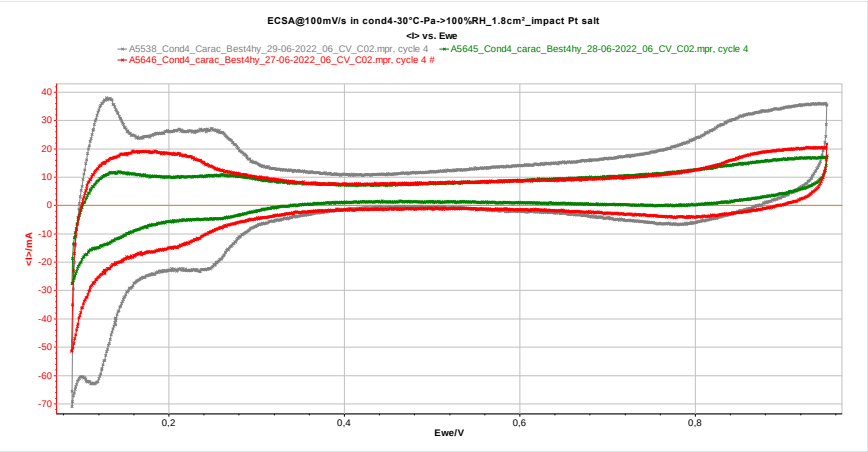


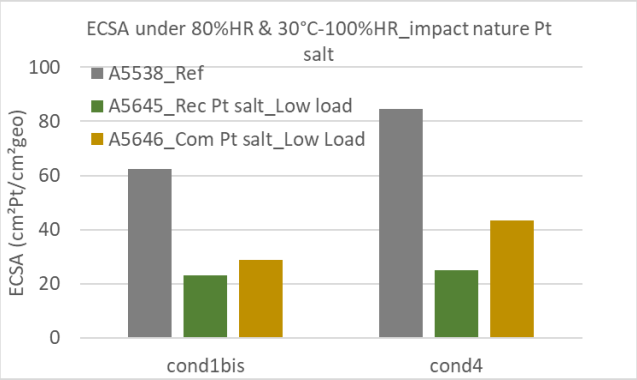


Electrochemical characterization: ESCA



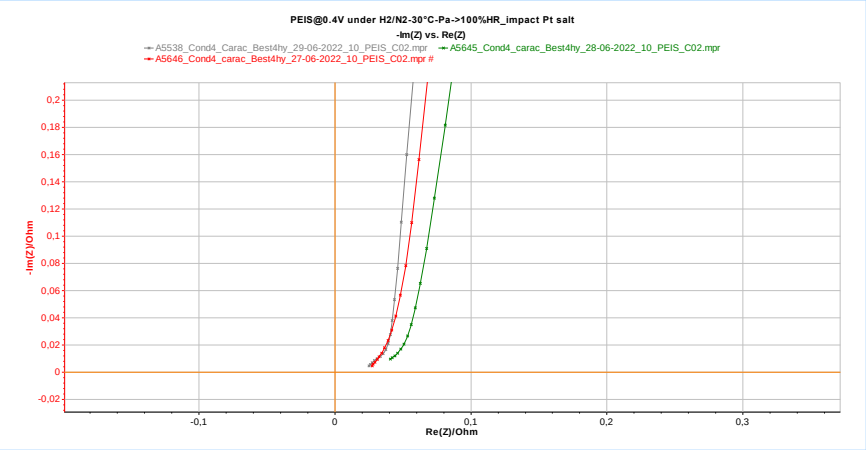
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

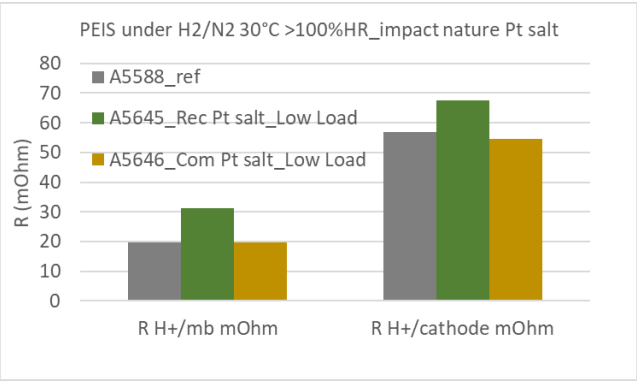




Electrochemical characterization under cond4-30°C-Pa->100%HR

PEIS@0.4V under H2/N2

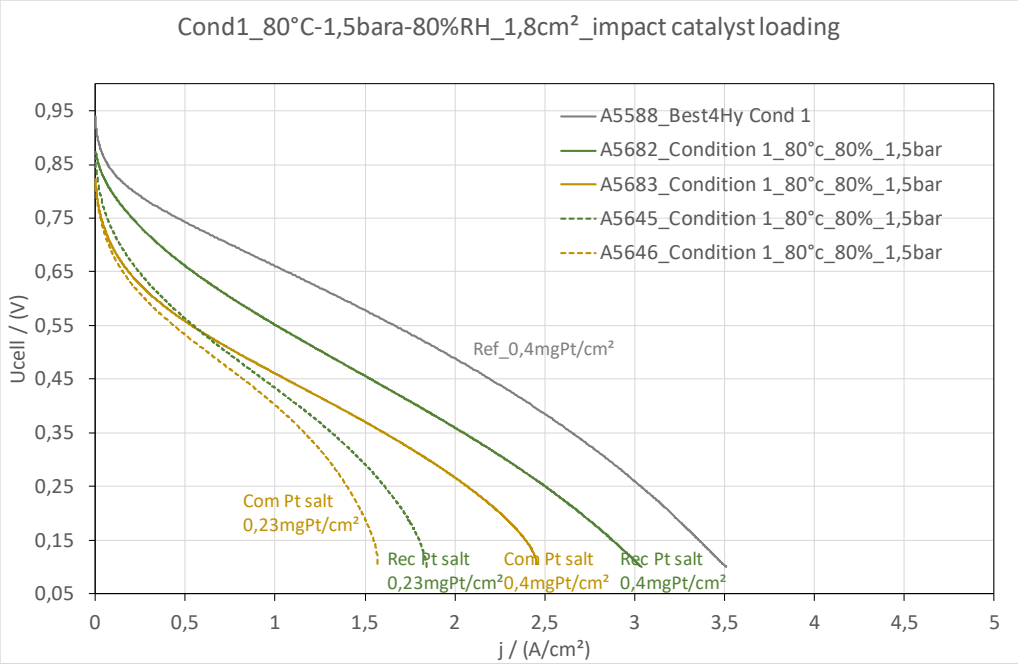


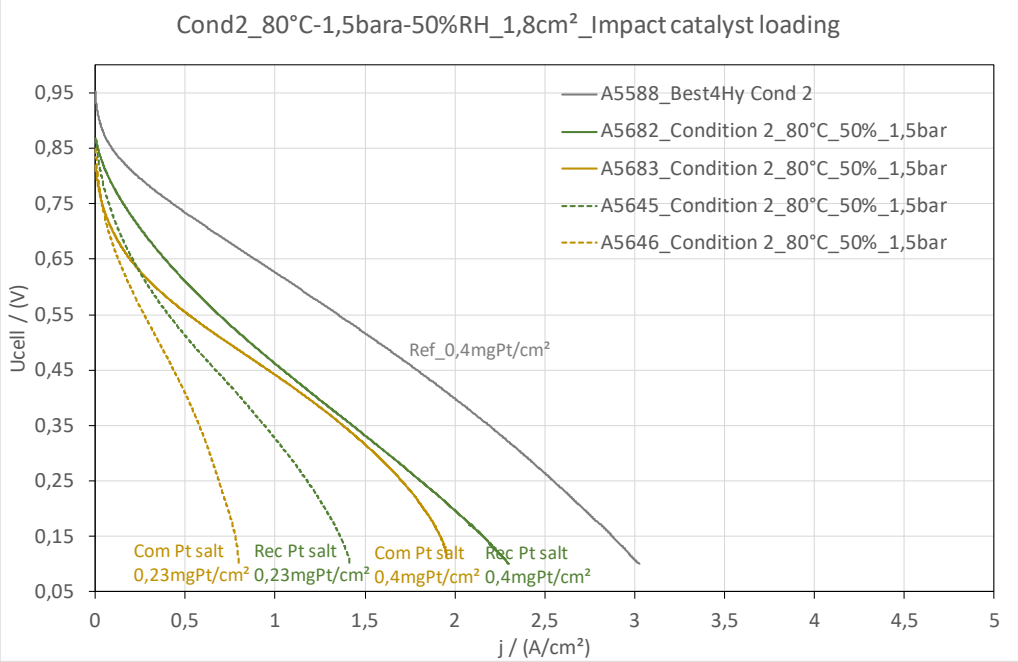


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

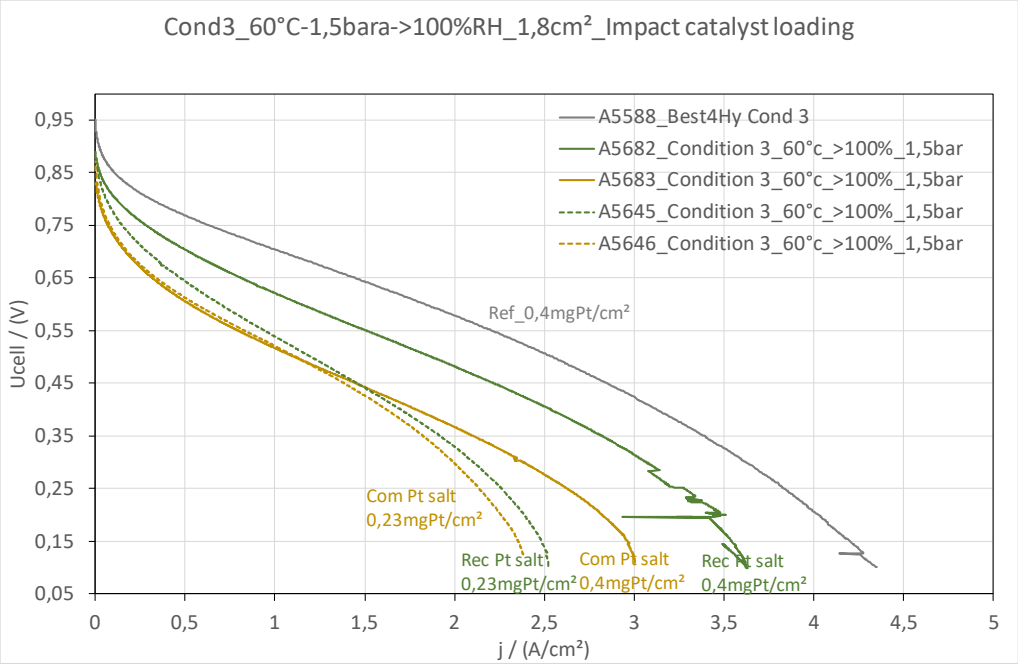
In 1.8cm²

Polarization curves



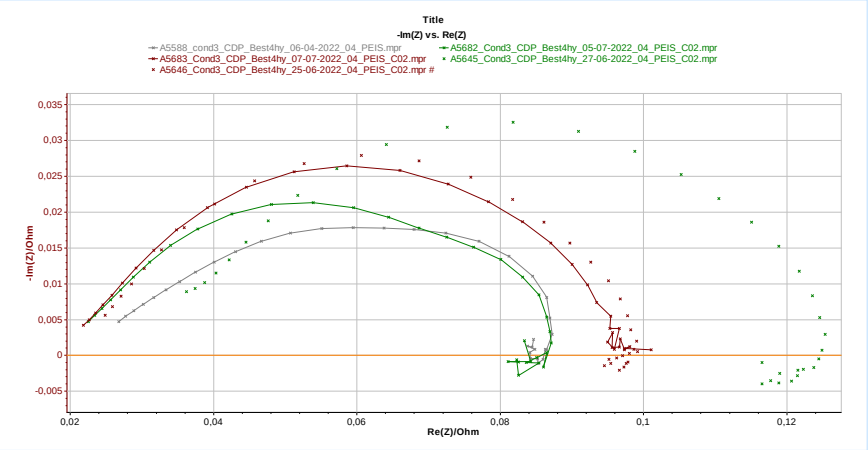


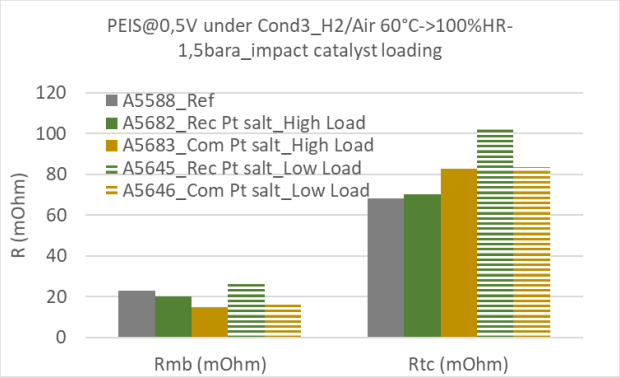
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



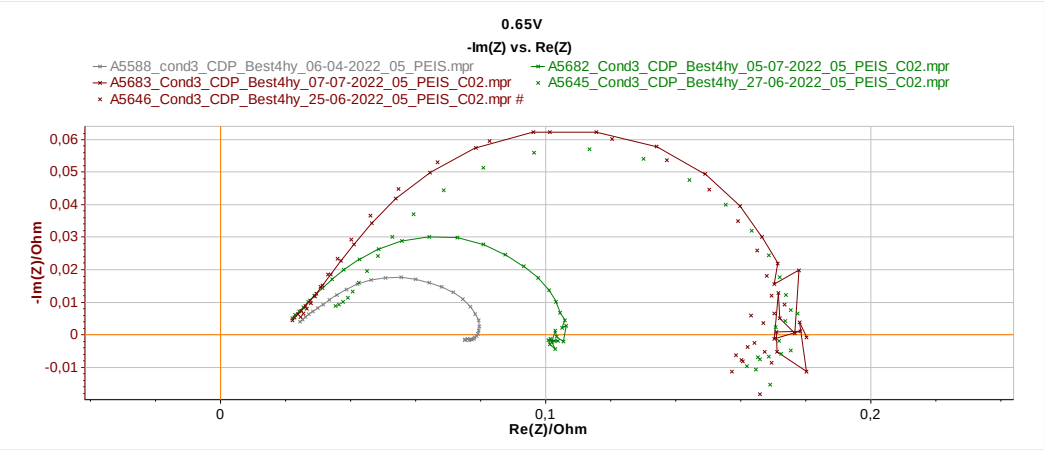
Electrochemical characterization under Cond3-H2/Air-60°C-1.5bara->100%RH

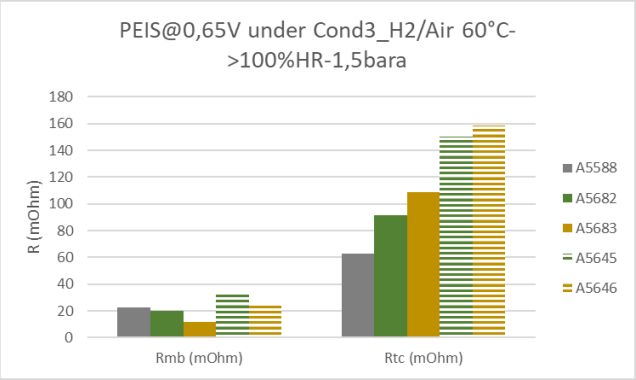
PEIS@0.5V and 0.65V



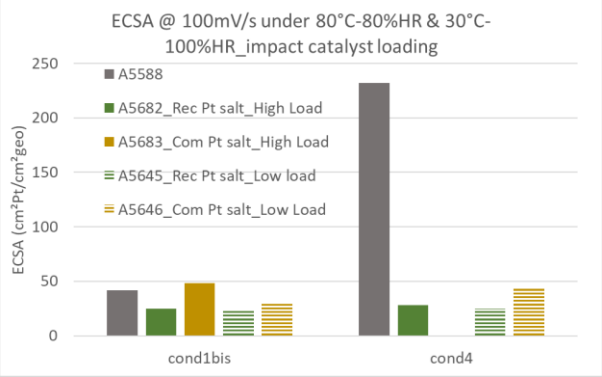


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



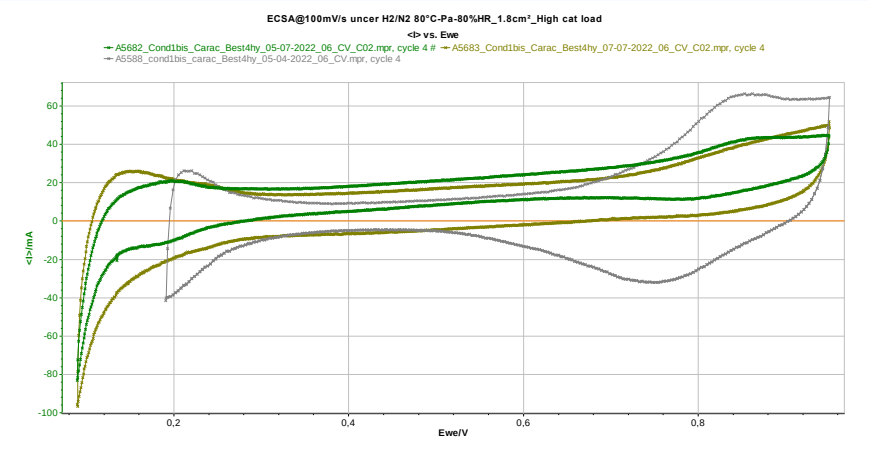


Electrochemical characterization: ESCA

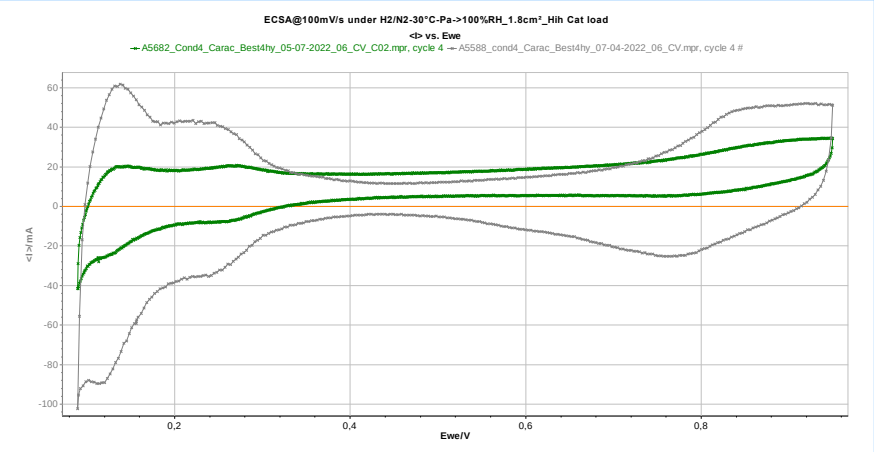


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

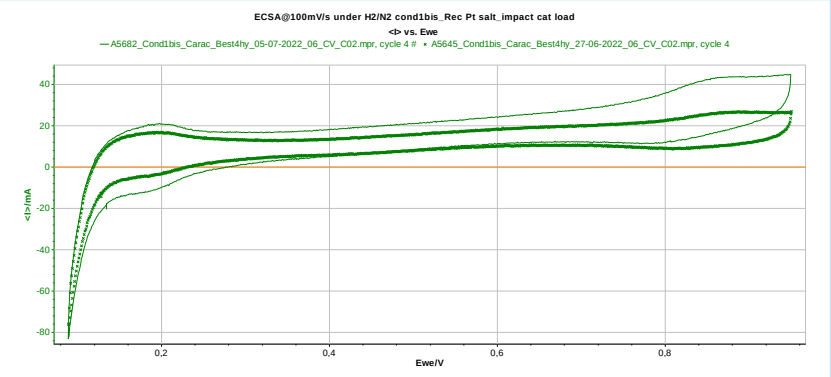
Impact of nature of Pt salt @ high catalyst loading, in cond1bis:



Impact of nature of Pt salt @ high catalyst loading, in cond4:

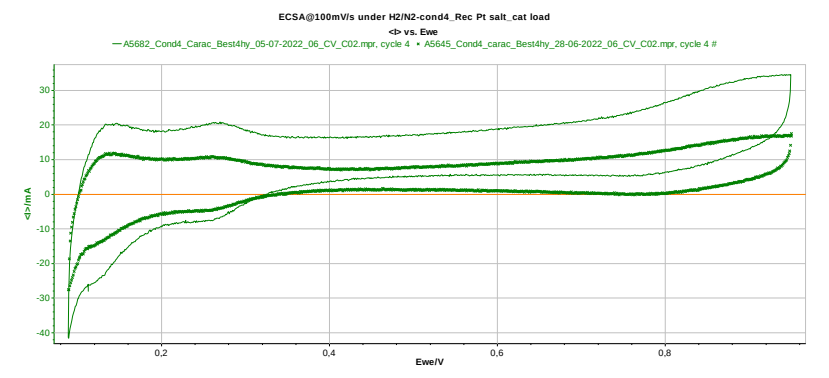


Impact of catalyst loading for Recycled Pt salt, in cond1bis:

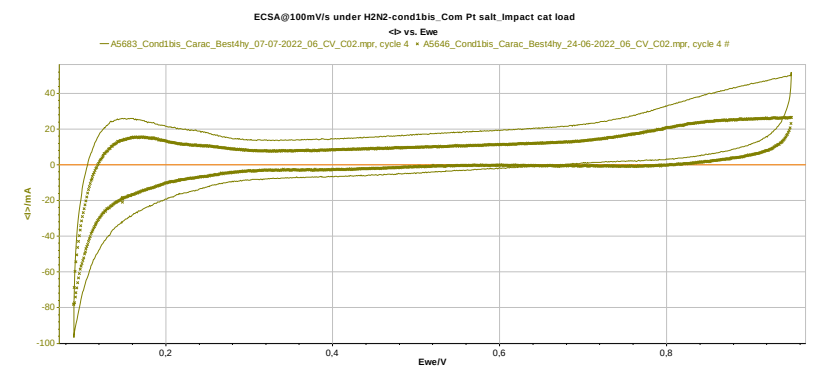


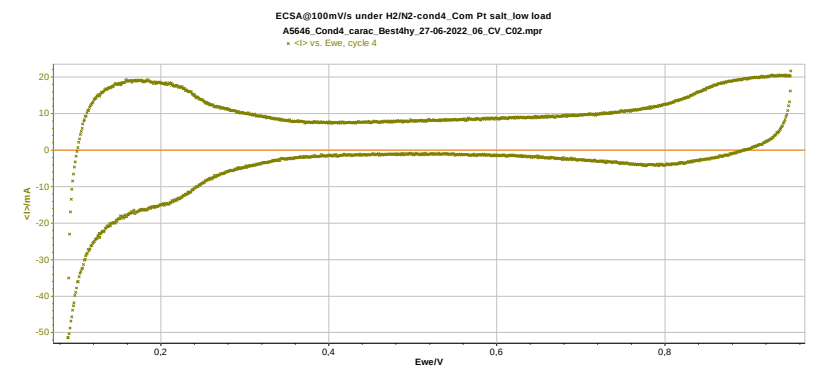
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Impact of catalyst loading for Recycled Pt salt, in cond4:

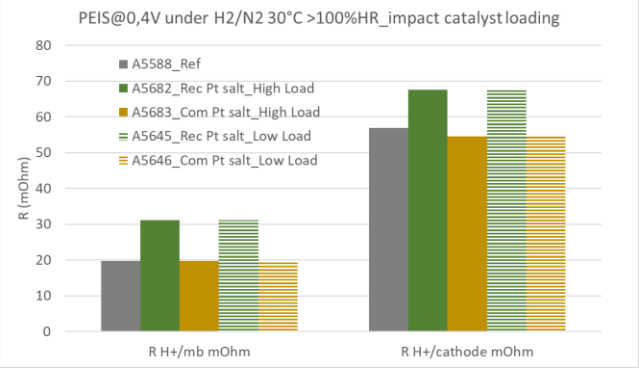


Impact of catalyst loading for Commercial Pt salt, in cond1bis:





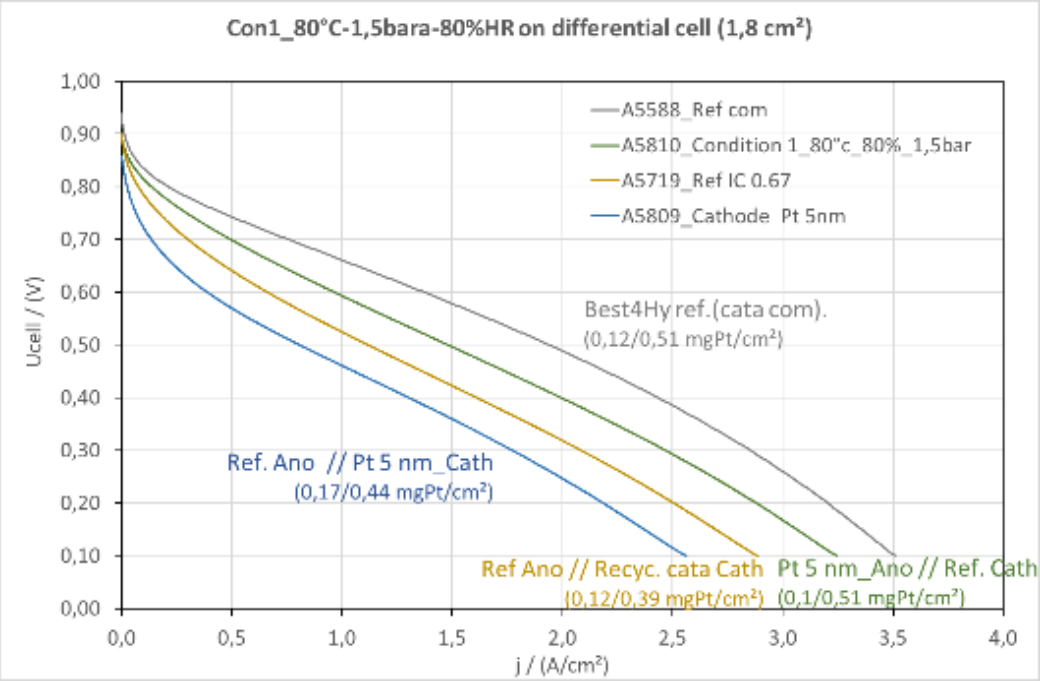
Impact of catalyst loading for Recycled Pt salt, in cond4:

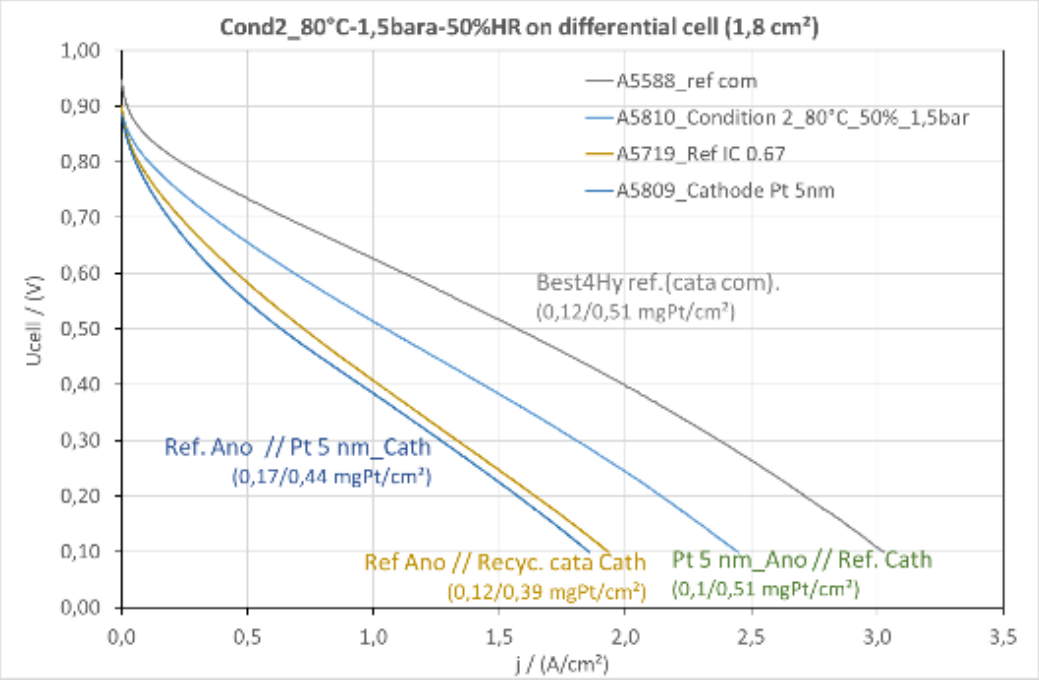


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

in 1.8cm²

Polarizations curves

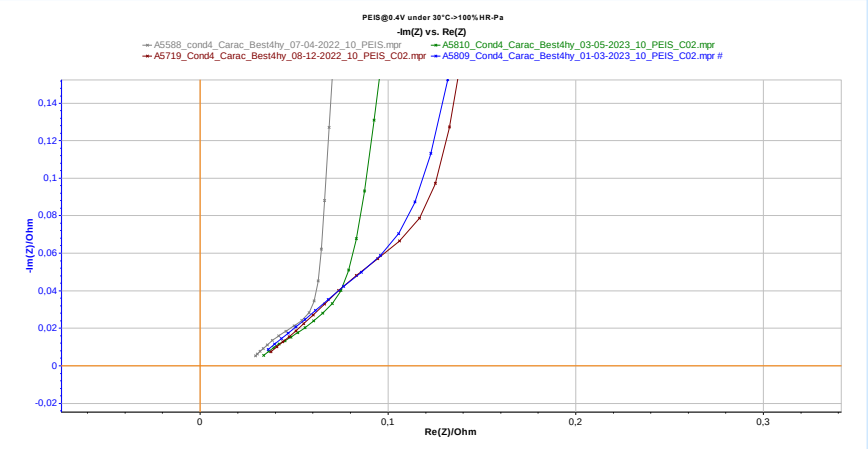


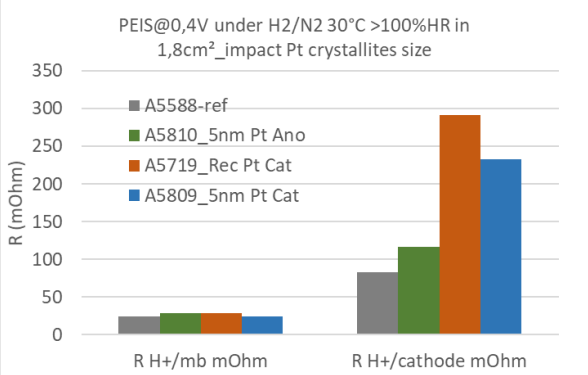


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

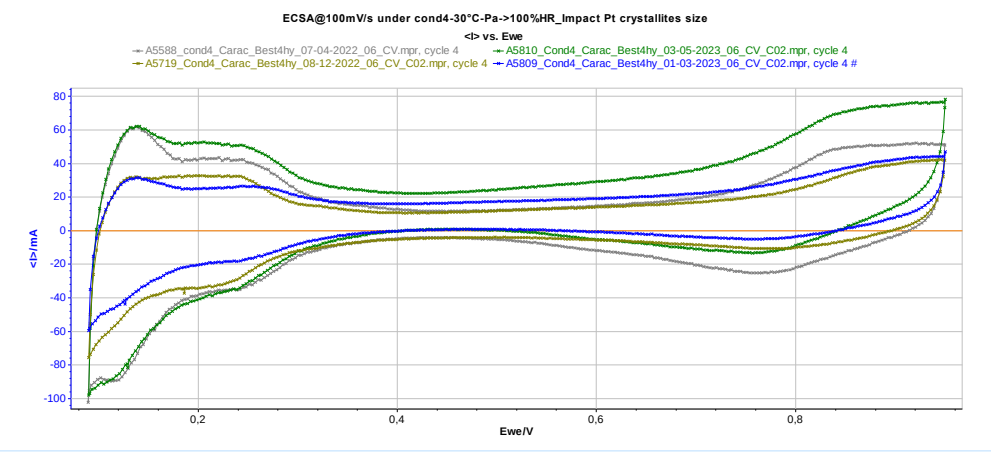
Electrochemical characterization under cond4-30°C-Pa->100%RH

PEIS@0.4V

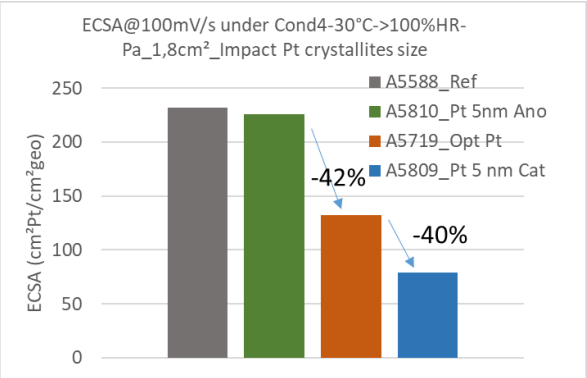


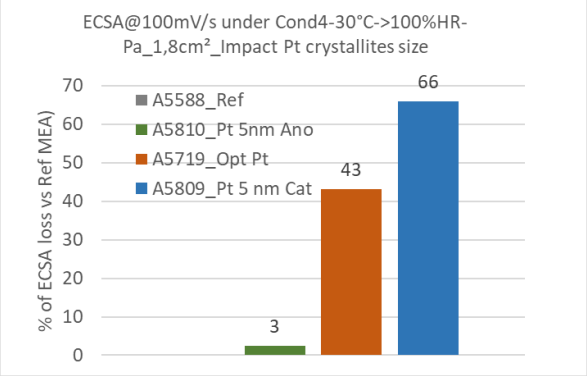


ECSA in cond4:

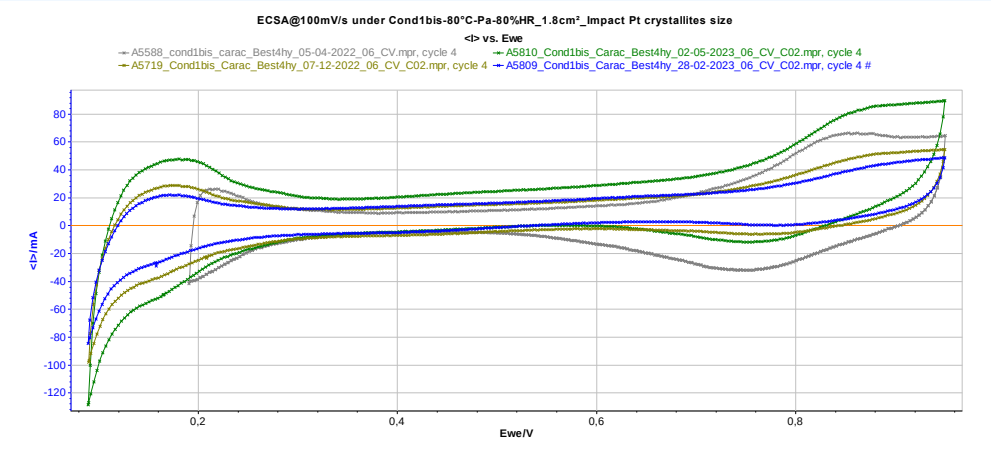


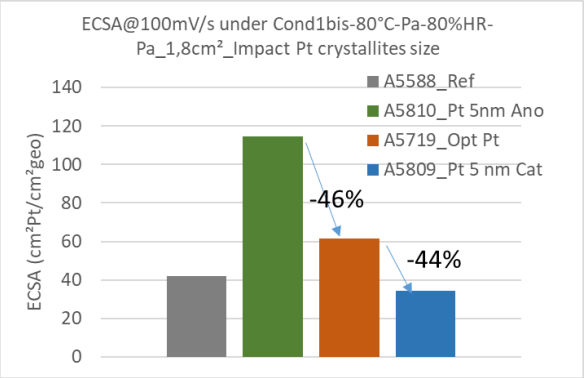
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.





ECSA in cond 1bis

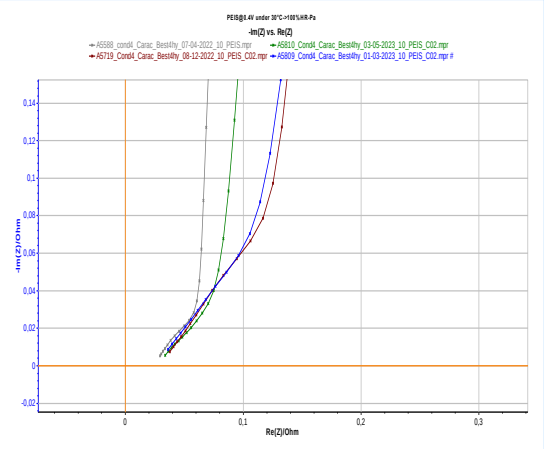


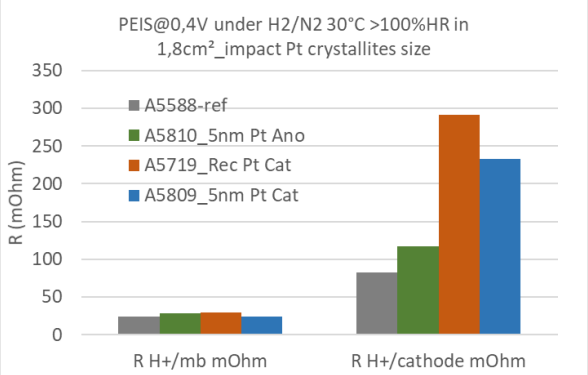


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under cond4-30°C-Pa->100%RH

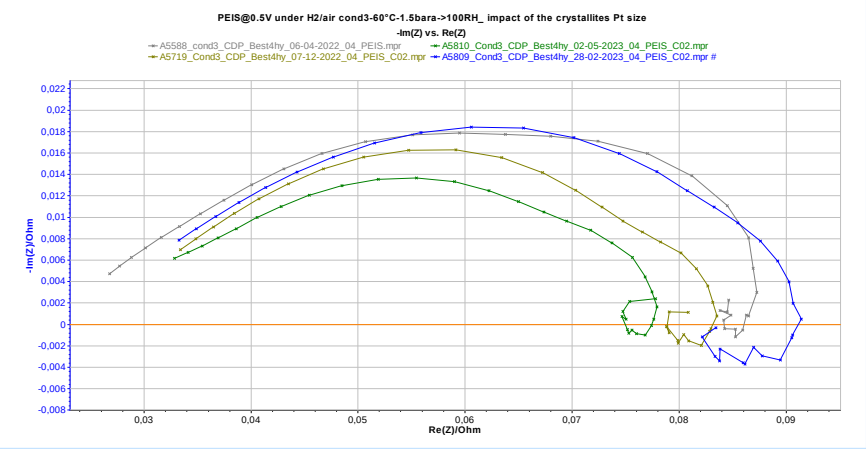
PEIS@0.4V



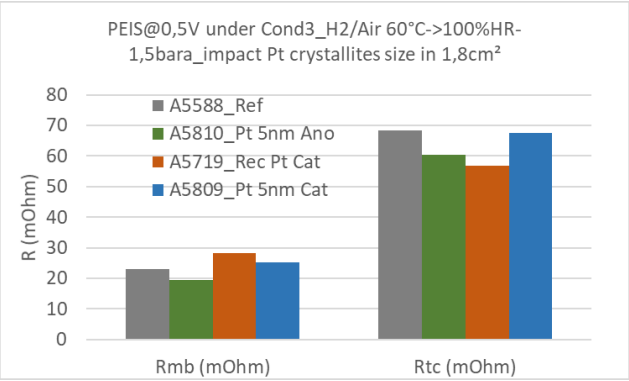


Electrochemical characterization under cond3-60°C-1.5bara->100%RH

PEIS@0.5V under H_2/air



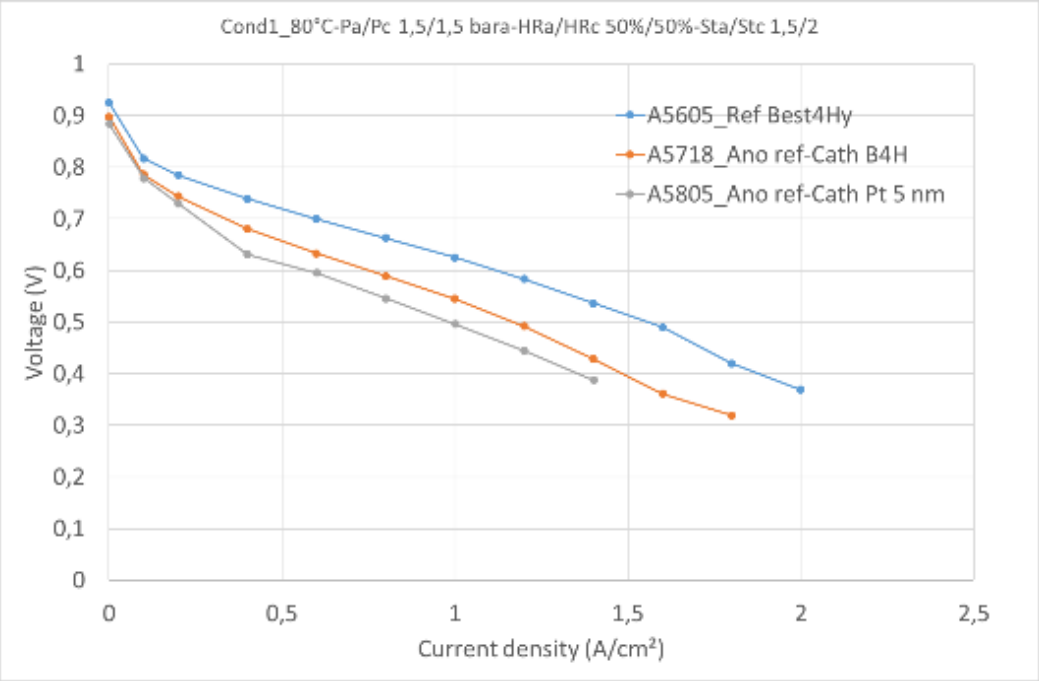
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

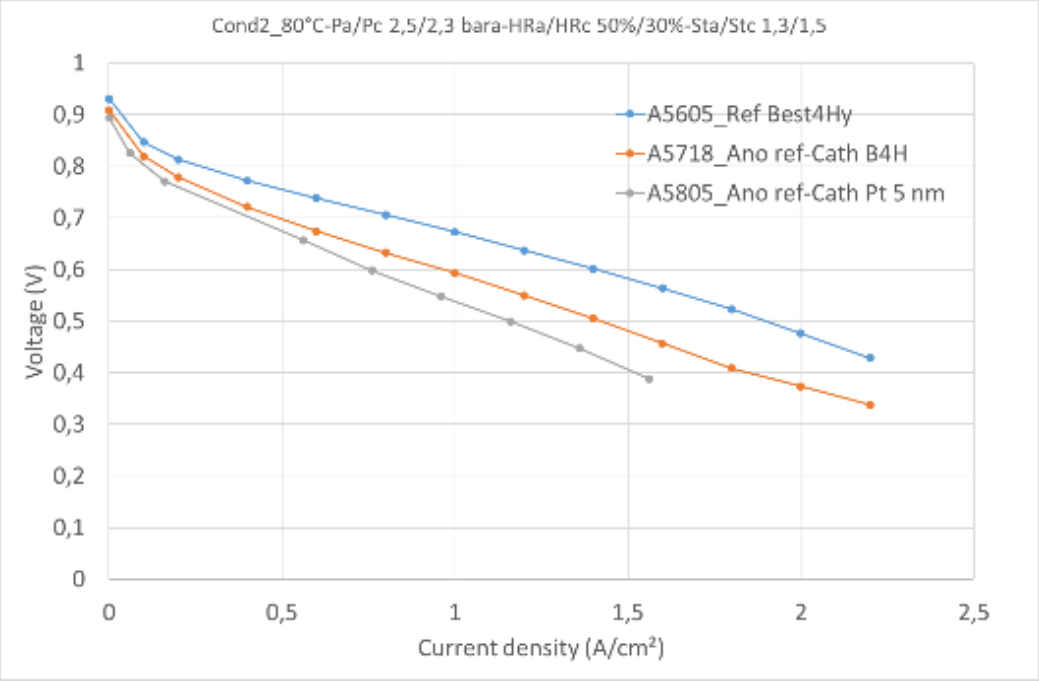


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

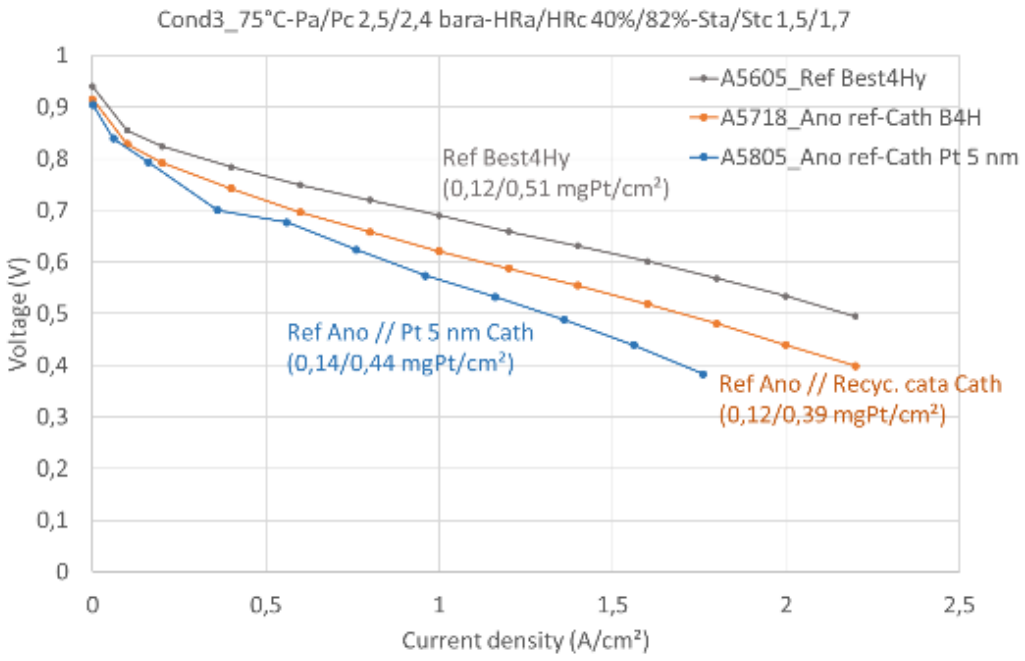
In 25cm²

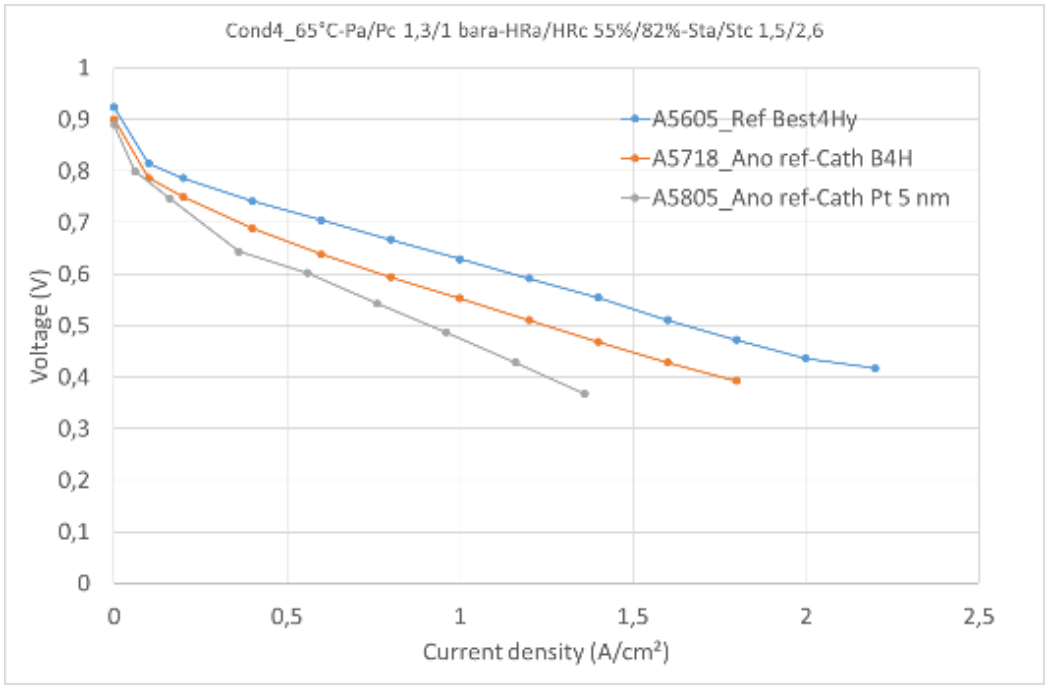
Polarization curves





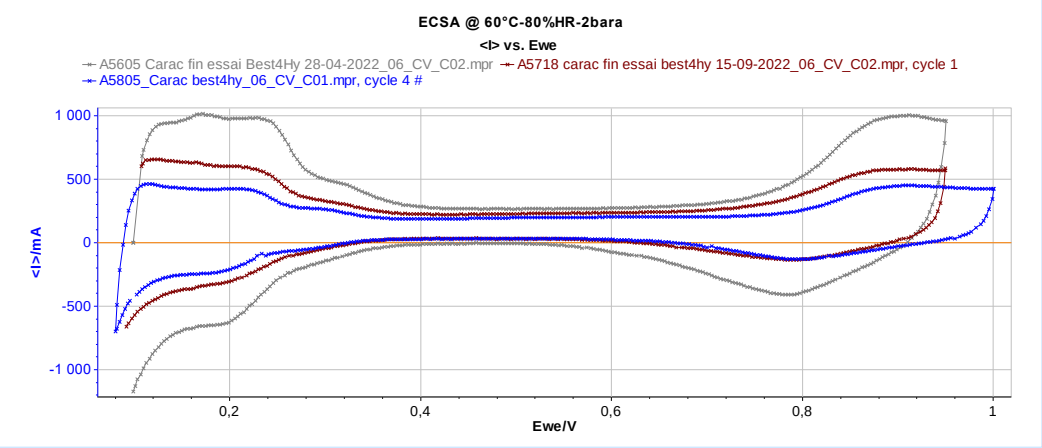
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

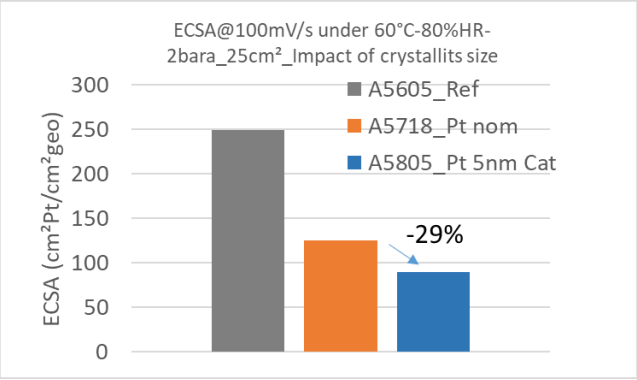


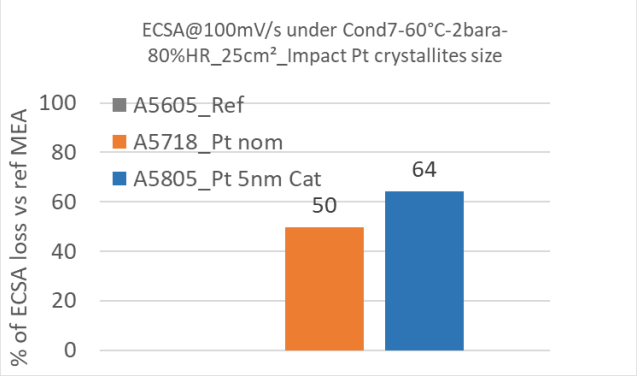


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under H2/N2-60°C-2bara-80%HR: ECSA

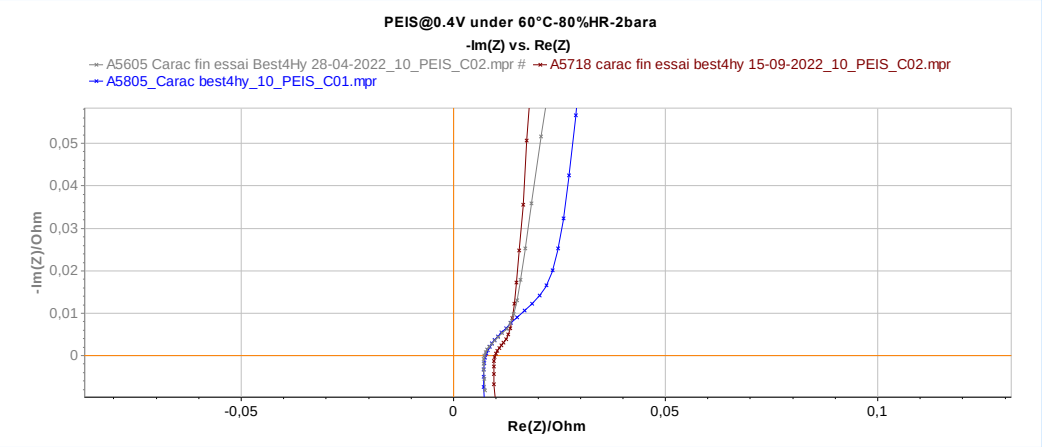


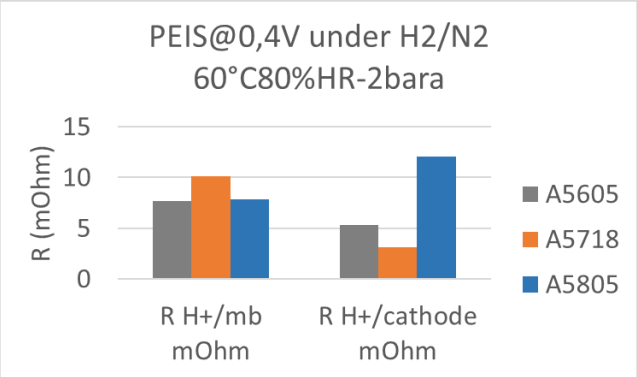




This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under H2/N2-60°C-2bara-80%HR: PEIS

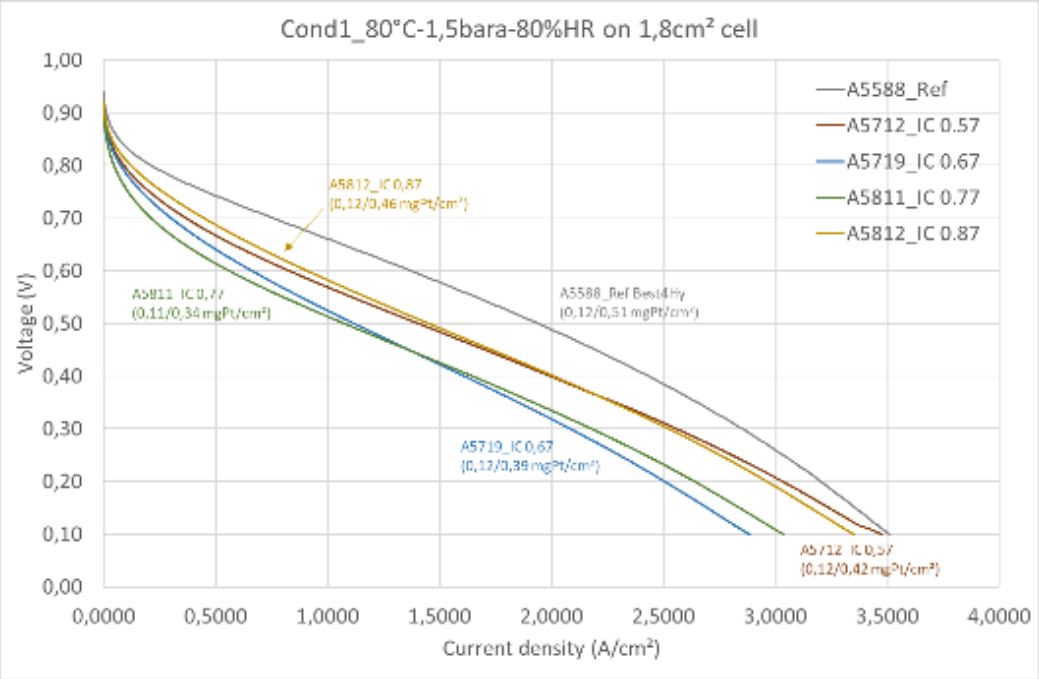


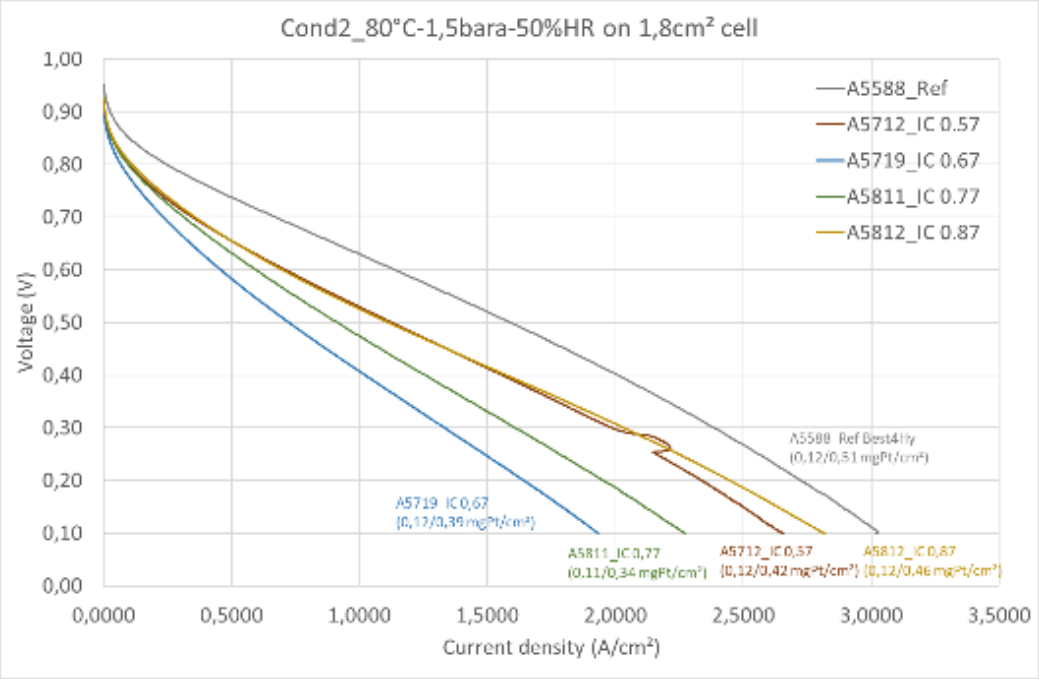


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

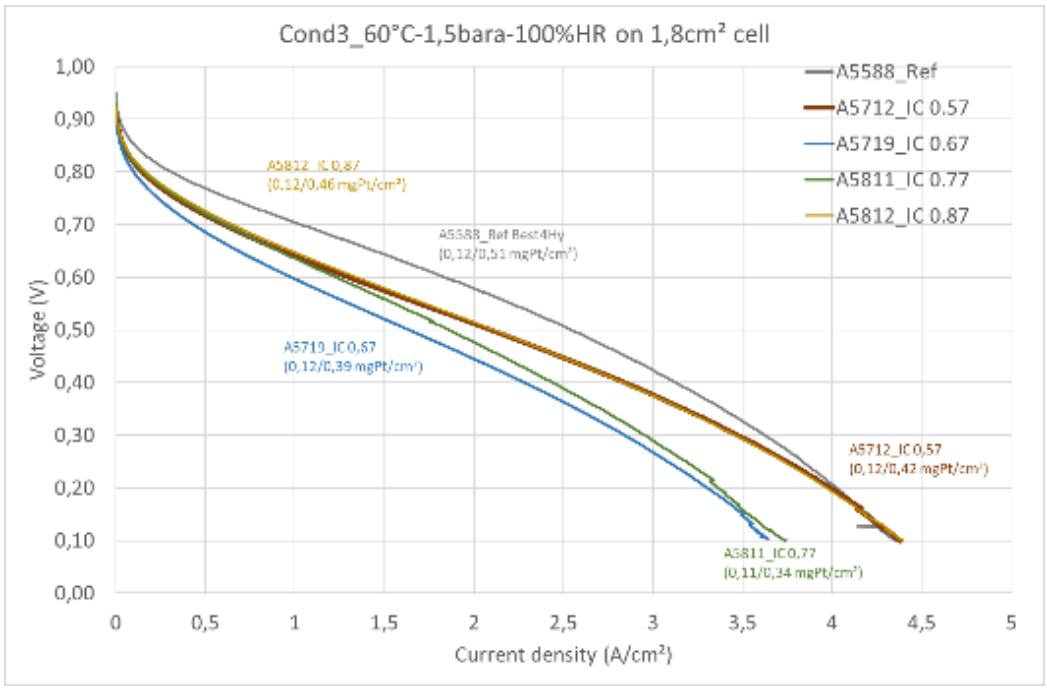
In 1.8cm²

Polarizations curves



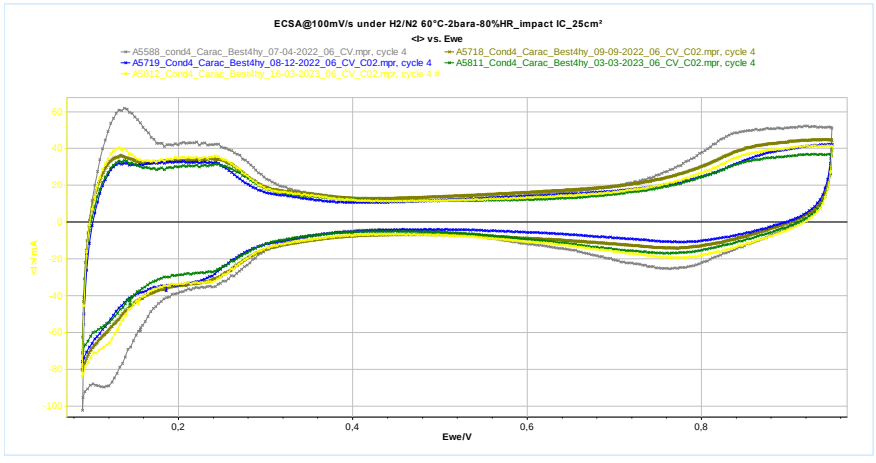


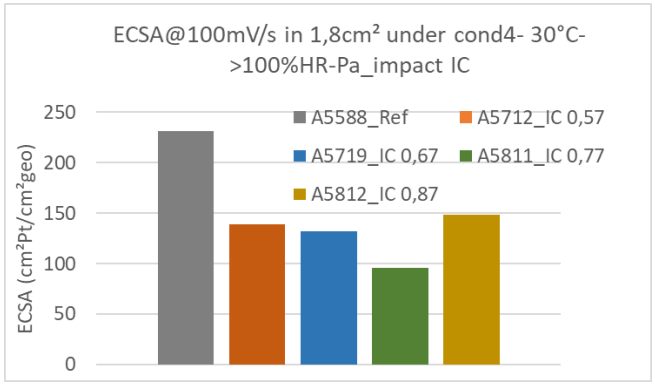
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



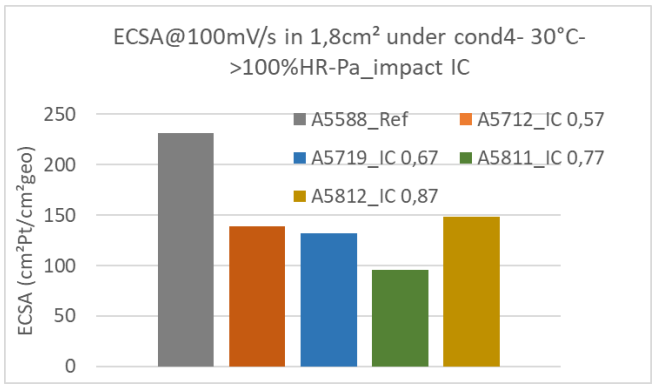
Electrochemical characterization under H2/N2-cond4 -30°C-Pa->100%RH:

ECSA



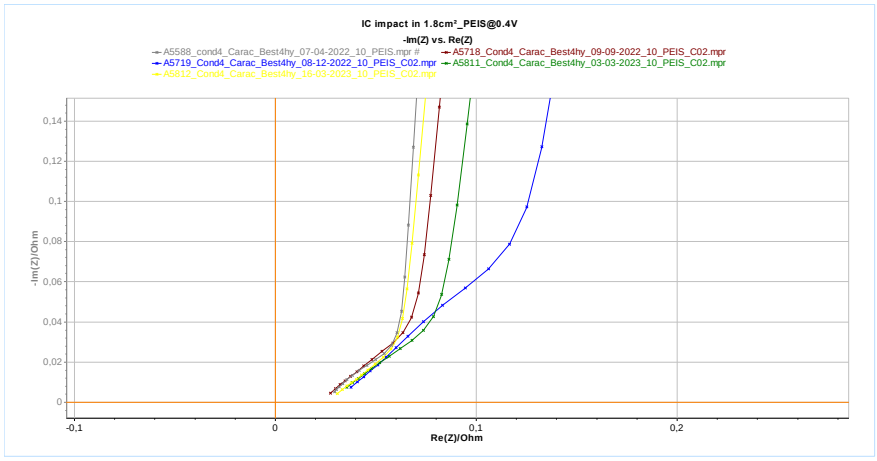


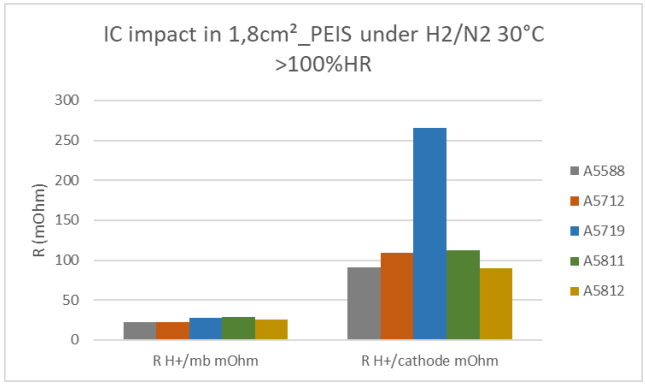
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



Electrochemical characterization under H2/N2-cond4 -30°C-Pa->100%RH

PEIS@0.4V under H2/N2

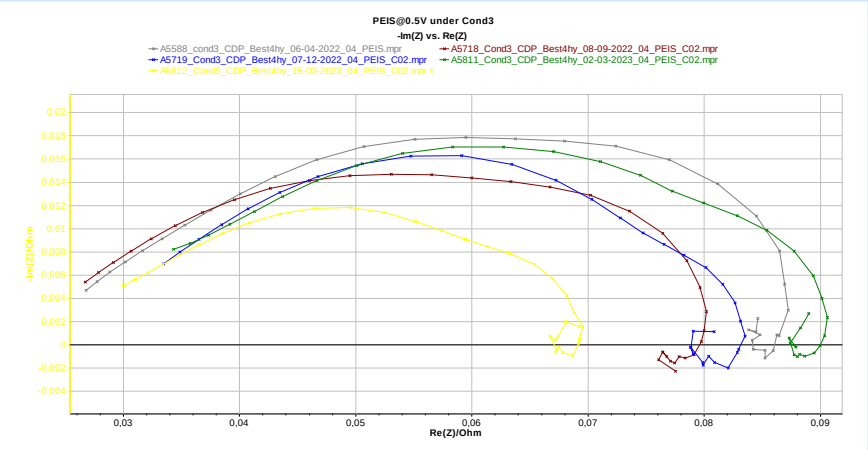


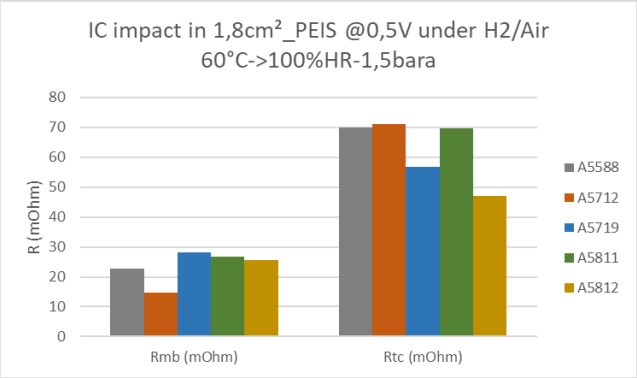


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization under H2/air-cond3 -60°C-1.5bara->100%RH

PEIS@0.5V under H2/air

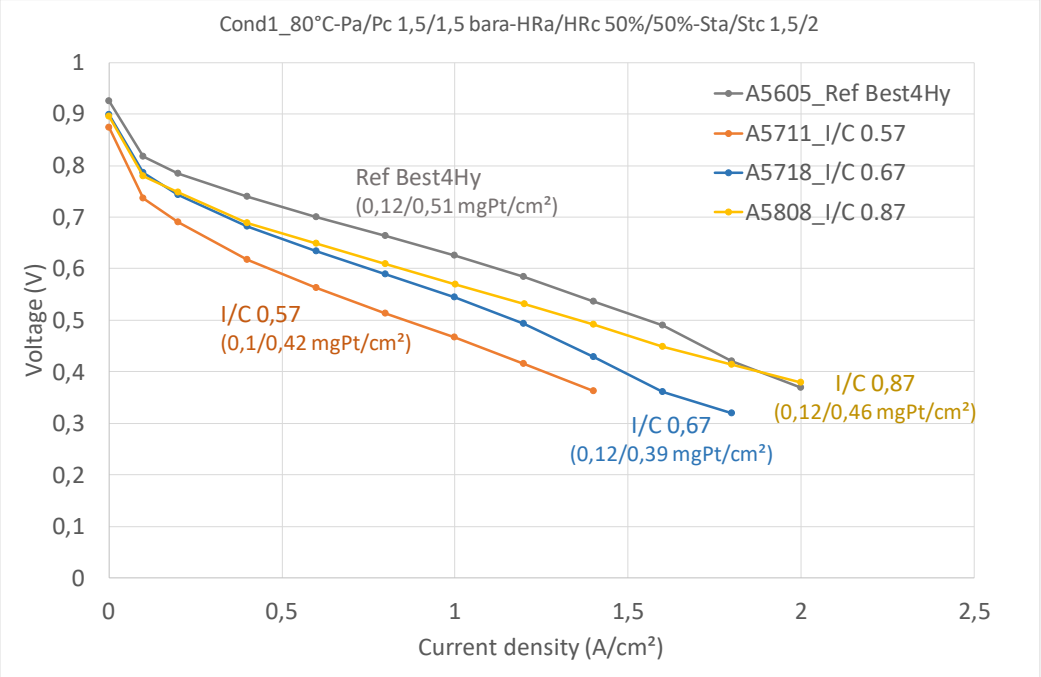


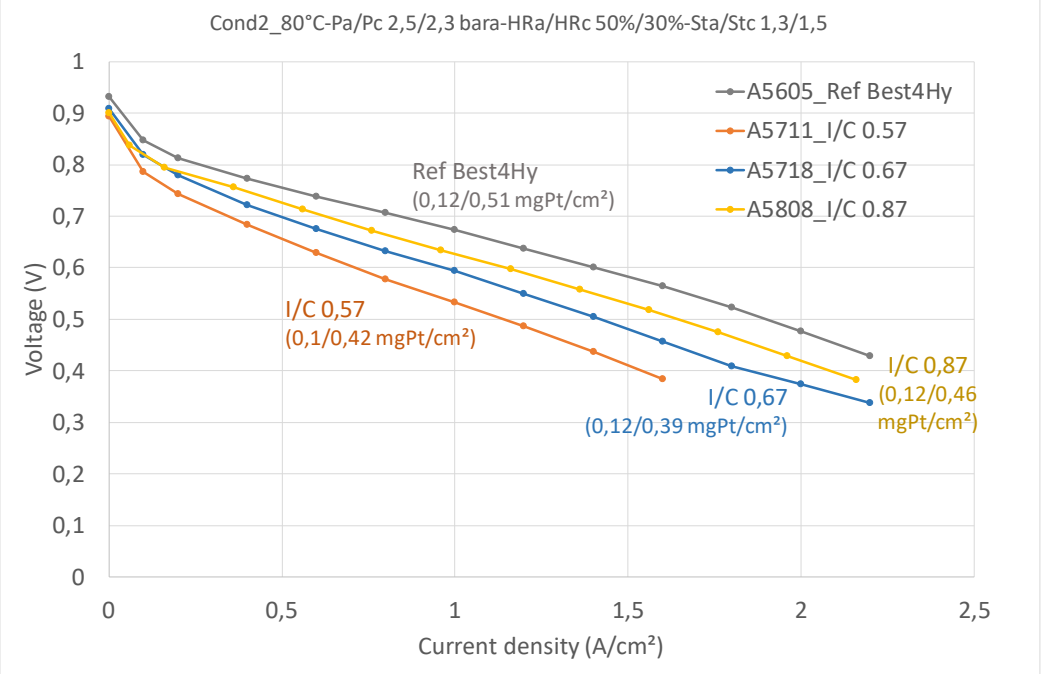


This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

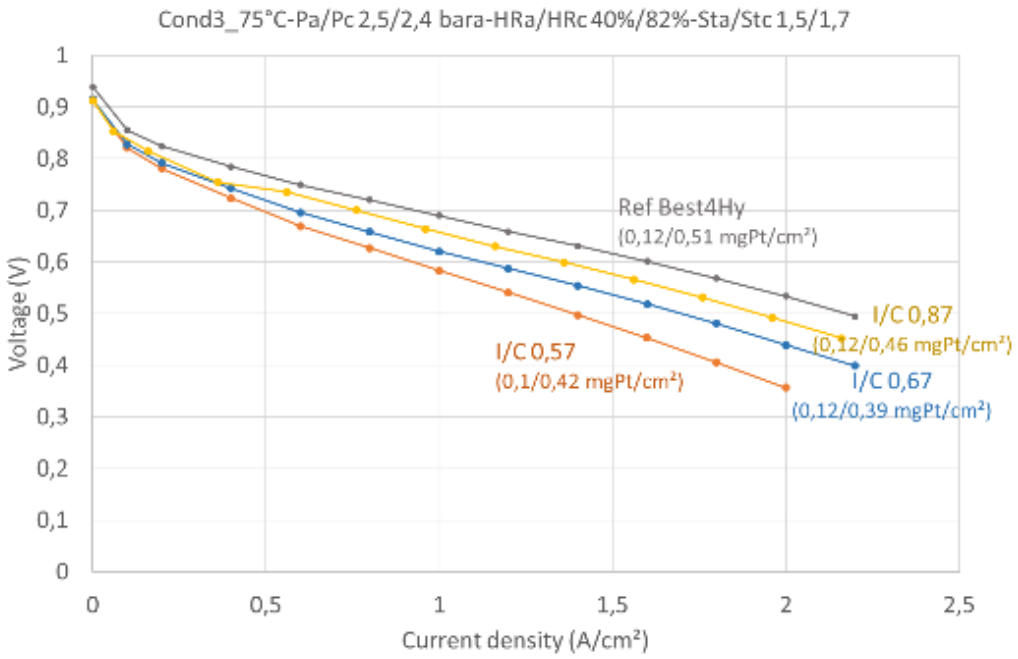
In 25cm² single cell

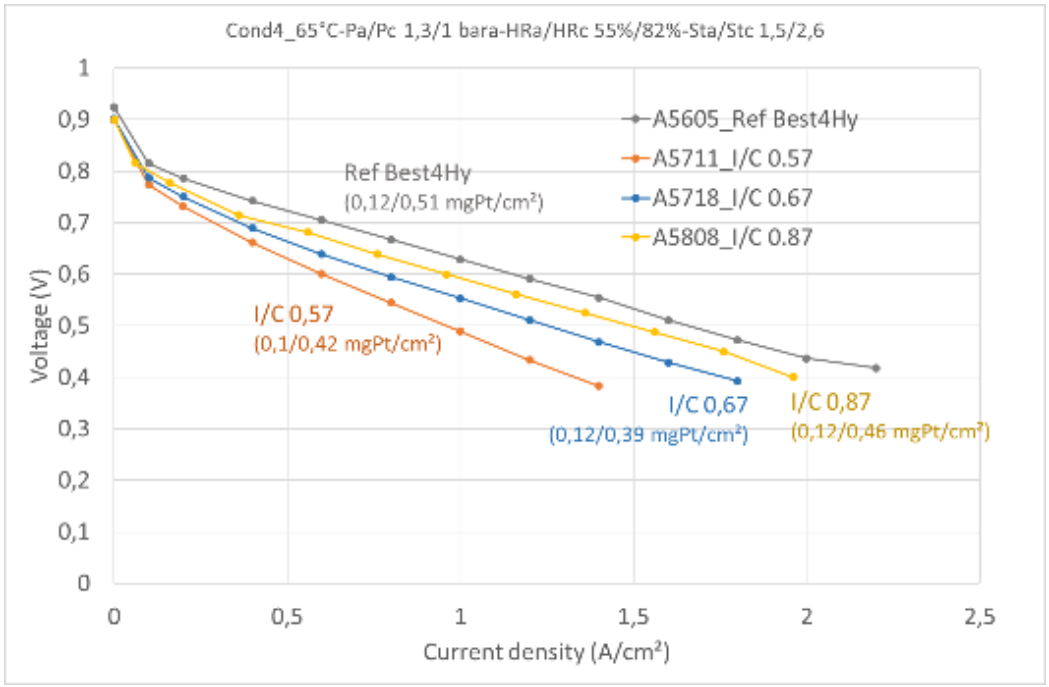
Polarizations curves





This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

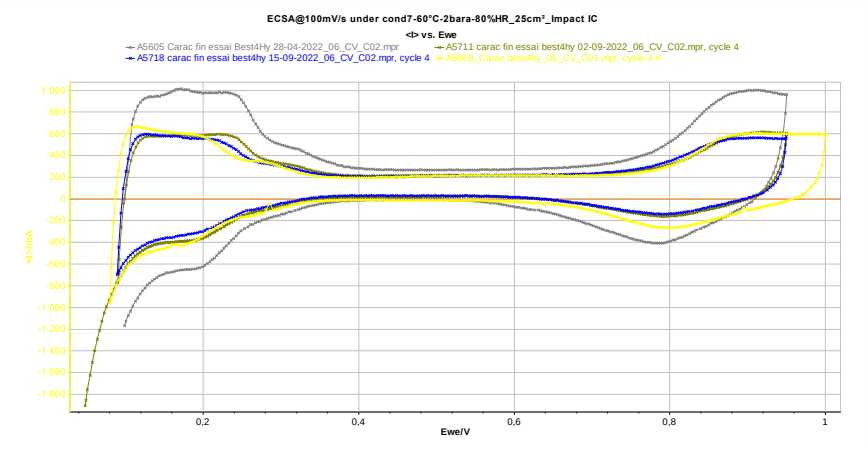


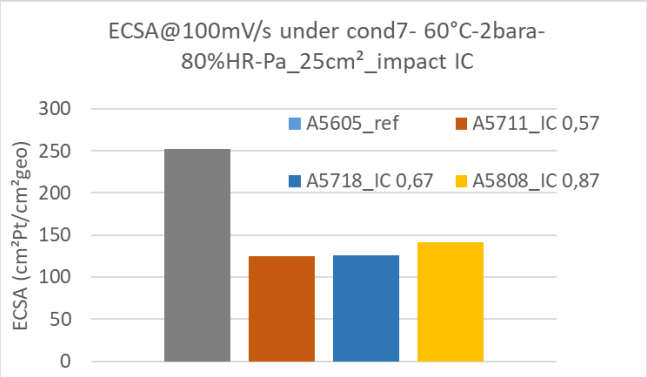


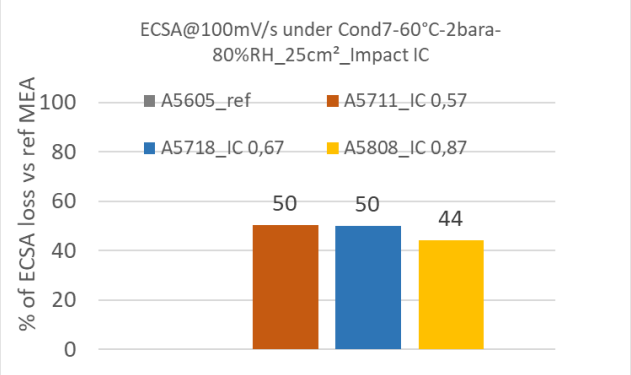
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

Electrochemical characterization H2/N2-60°C-2bara-80%HR:

ECSA



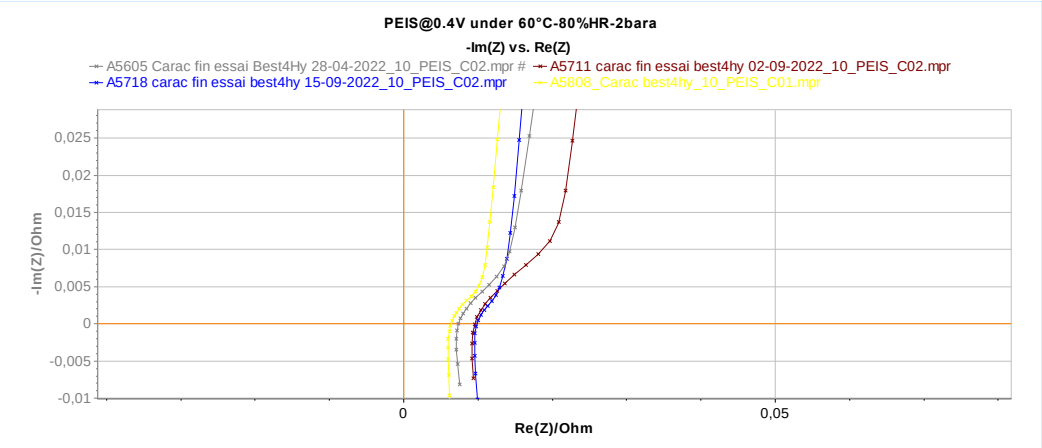


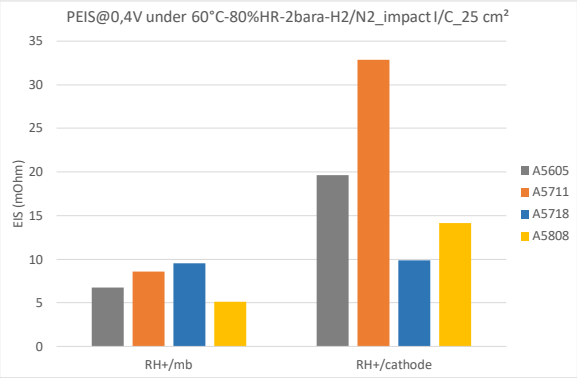


Electrochemical characterization H2/N2-60°C-2bara-80%HR

PEIS@0.4V

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.





This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.