



Cost-effective PROton Exchange MEMbrane WaTer Electrolyser for Efficient and Sustainable Power-to-H2 Technology

Grant No. 862253

Start date: 01.04.2020 – Duration: 36 months

Project Coordinator: Daniel García-Sánchez - DLR

D2.4: 2nd annual report on MEA performance assessment

WP2 Membrane and MEA development

WP Leader: FZJ

Deliverable Responsible: CNR

Deliverable Author(s): Stefania Siracusano, Antonino Aricò (CNR); Nikolai Utsch, Meital Shviro (FZJ)

Status: F

(D: Draft, FD: Final Draft, F: Final)

Dissemination level: PU

(PU: Public, CO: Confidential,

only for Consortium members (including the Commission Services))



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862253

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862253.

Despite the care that was taken while preparing this document the following disclaimer applies: the information in this document is provided as is and no guarantee or warranty is given that the information is fit for any particular purpose. The user thereof employs the information at his/her sole risk and liability.

The document reflects only the authors' views. The European Union is not liable for any use that may be made of the information contained therein.

Document history

Version Number	Date of issue	Author(s)	Brief description of changes
V 01	15/12/2021	Stefania Siracusano (CNR)	Creation of draft
V 02	11/01/2022	Nikolai Utsch, Meital Shviro (FZJ)	2 nd version
V 03	17/01/2022	Stefania Siracusano, Antonino Aricò (CNR)	Implementation, 3 rd version
V 04	18/01/2022	Stefania Siracusano (CNR)	Final version

Table of Content

Document history	3
List of Figures	5
List of Tables	6
Acronyms	7
Executive Summary	8
1 Introduction	9
2 MEA performance assessment: <i>CRM free catalysts</i>	10
2.1 MEA preparation	10
2.2 MEA electrochemical characterization	10
3 MEA performance assessment: <i>reduced CRM catalysts</i>	13
3.1 MEA preparation	13
3.2 MEA electrochemical characterization	13
4 Cross-over measurement	19
Acknowledgement	24

List of Figures

Figure 1. Polarization curves for selected non-CRM anode and cathode electrocatalysts based MEA. Raw and IR-free corrected curves

Figure 2.1 EIS for selected non-CRM anode and cathode electrocatalysts based MEA at 2 V and 80°C

Figure 3. Chrono-potentiometric test at 0.2 A·cm⁻² and 80 °C for selected non-CRM anode and cathode electrocatalysts based MEA

Figure 4. Recorded single-cell testing performance for different loaded Pt@Mo MEAs

Figure 5. Occurring hysteresis for all Pt@Mo-based MEA indicating non-stable cathode

Figure 6. Backside of the membrane after spraying the catalysts as layer on top (a) and impact of required hydration step on electrode stability (b)

Figure 7. Single-cell testing results for different loaded Ir-ATO catalysts compared against benchmark catalysts

Figure 8. Results from durability study with (a) polarization curves at BOT & EOT as well as (b) monitored current density for 250h durability test at 2V with dip at 65h caused by the test station

Figure 9. Testing the durability of low loadings with Ir-ATO 50 wt.% as anode catalyst deployed on N117 and NDP8003

Figure 10. Single-cell testing results for different loaded Ir perovskite catalysts compared against benchmark catalysts

Figure 11. Testing durability of 0.4 mgIr/cm⁻¹ with Ir perovskite as anode catalyst at a current density of 2 A/cm⁻² during 450 h

Figure 12. Polarization curves of different membranes tested at FZJ

Figure 13. Cross-over measurement in single-cell assembly tested at FZJ

Figure 14. Cross-over monitored at 3.5 A·cm⁻² for 250h of operation using ND8003 and N117

Figure 15. Polarization curves and ac-impedance of N212, ND8003 and N117 based MEAs tested at CNR-ITAE

Figure 16. H₂ crossover in O₂ of N212, ND8003 and N117 based MEAs tested at CNR-ITAE

List of Tables

Table1: membranes characteristics tested in single cell

Acronyms

BET - Brunauer Emmett-Teller

CRM – Critical raw material

CV - Cyclic Voltammetry

ECSA- Electro chemical surface area

EDX- Energy-dispersive X-ray

EIS- Electrochemical Impedance Spectroscopy

HER- Hydrogen Evolution Reaction

ICP- Inductively Coupled Plasma

OER- Oxygen Evolution Reaction

OCP- Open circuit potential

MEA- Membrane electrode assembly

PEM- Proton Exchange Membrane

PEMWE- Proton exchange membrane water electrolysis

RDE -Rotating Disk Electrode

RHE- Reversible Hydrogen Electrode

SEM- Scanning Electron Microscopy

TEM -Transition Electron Microscopy

XPS- X-ray Photoelectron Spectroscopy

XRD- X-ray Diffraction

XRF – X-Ray fluorescence spectroscopy

WE - Working Electrode

Executive Summary

The deliverable D2.4 "2nd annual report on MEA performance assessment" provides the main results obtained with the CRM free catalysts and the reduced CRM catalysts-based MEAs in terms of performance and stability obtained in PEM electrolysis single test. The overall performance and durability for single cell were obtained by steady-state polarization curves, EIS and constant durability protocols. In addition, to evaluate H₂ crossover through the membranes, in-situ gas crossover measurements have been carried out by FZJ and CNR.

1 Introduction

Water electrolysis is a very promising technology for sustainable hydrogen generation using renewable electrical energy. The excellent performance and dynamic behavior for storing electrical energy in hydrogen allows polymer electrolyte membrane (PEM) electrolysis to cover the gap between the intermittent renewable power production and the grid demand at different time horizons and scales. To allow for a widespread utilisation of the PEM electrolysis technology, a significant reduction of the capital costs is strongly necessary. To achieve such objective, precious metal catalysts used in the electrolysis systems should be minimised.

The main objective of WP2 is to develop advanced, highly efficient and durable membrane electrode assemblies (MEAs) through the integration the novel electro catalysts developed in the WP1, based on reduced CRM or free catalysts, and new durable membranes developed within WP2.

Deliverable D2.4: "2nd annual report on MEA performance assessment" provides the main results obtained with the CRM free catalysts and the reduced CRM catalysts based MEAs in terms of performance and stability obtained in PEM electrolysis single cells.

2 MEA performance assessment: CRM free catalysts

2.1 MEA preparation

A Nafion 212 membrane was used for the test in single cell with the total CRM free catalysts based MEA. An Ag/Ti-suboxide (30:70), prepared by CNR ITAE, was used as anode catalyst. The ink composed of 80 wt.% catalyst and 20 wt. % Nafion ionomer (5 wt.% Ion Power solution) in deionised water and anhydrous absolute ethanol alcohol (Carlo Erba) was prepared by mixing under ultrasounds. The slurry was directly deposited by using a spray coating technique onto a Titanium fiber mesh, 300 μm thick, characterized by about 70 % porosity. The anode loading resulted 12 $\text{mg}\cdot\text{cm}^{-2}$. CS/C has prepared MoS_2 dispersed onto an active carbon (Black Pearls), as CRM-free electrocatalyst for the hydrogen evolution reaction. This MoS_2/BP catalyst was mixed with 15 wt. % of Nafion ionomer, deionised water and anhydrous absolute ethanol alcohol (Carlo Erba) in order to produce the ink for the spray deposition of cathode catalyst. This ink was spread onto carbon cloth backing (GDL HT carbon, 300 μm thick carbon cloth) with a Pt loading of 0.5 $\text{mg}\cdot\text{cm}^{-2}$. The cathode loading was 1.6 $\text{mg}\cdot\text{cm}^{-2}$. The MEA was prepared by a hot-pressing procedure by lamination at 130 $^\circ\text{C}$ for 2 min at 3 KN of pressure. The electrolysis cell housing, where MEAs were assembled, consisted of a titanium plate at the anode side and a graphite plate at the cathode side. The active area (geometrical electrode area) of the MEA was 5 cm^2 .

2.2 MEA electrochemical characterization

Performance and stability of MEA was investigated at a temperature of 80 $^\circ\text{C}$ and under ambient pressure conditions. Deionised water, milli-Q Integral, Millipore ($\sim 0.05 \mu\text{S}$), further purified by an ion exchange resin cartridge, was recirculated by a pump at a flow rate of 1 $\text{ml min}^{-1} \text{cm}^{-2}$ at the anode side. Polarization curves (cell potential as a function of current density) and electrochemical impedance spectroscopy (EIS) were carried out by a PGSTAT Autolab 302 Potentiostat/Galvanostat equipped with a booster of 20 A (Metrohm) and a Frequency Response Analyser (FRA). The EIS measurements were performed under potentiostatic control in a frequency range between 20 kHz and 0.1 Hz by frequency sweeping in the single sine mode. The amplitude of the sinusoidal excitation signal was 10 mV root-mean-square (rms) excitation voltage. The series resistance was determined from the high frequency intercept on the real axis in the Nyquist plot. A cut-off voltage of 2.5 V was used for polarisation curves, while the impedance measurements were carried out at 1.8 V in order to evaluate the response in the activation-controlled region.

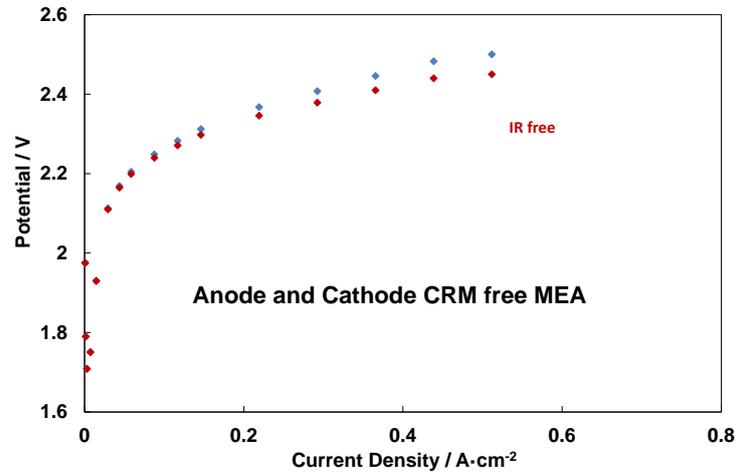


Figure 2. Polarization curves for selected non-CRM anode and cathode electrocatalysts based MEA. Raw and IR-free corrected curves

The single cell performance with an MEA totally based on CRM free-catalysts is relatively low and characterised by a strong activation control as consequence of their poor intrinsic catalytic activity compared to precious metal electrocatalysts. In order to improve the catalytic activity of the Ag/Ti-suboxide catalyst milled (30-70) and MoS₂/BP, optimization strategies and further investigation is planned, such as an increased amount of H₂ concentration during the heat treatment for the Ag/Ti-suboxide.

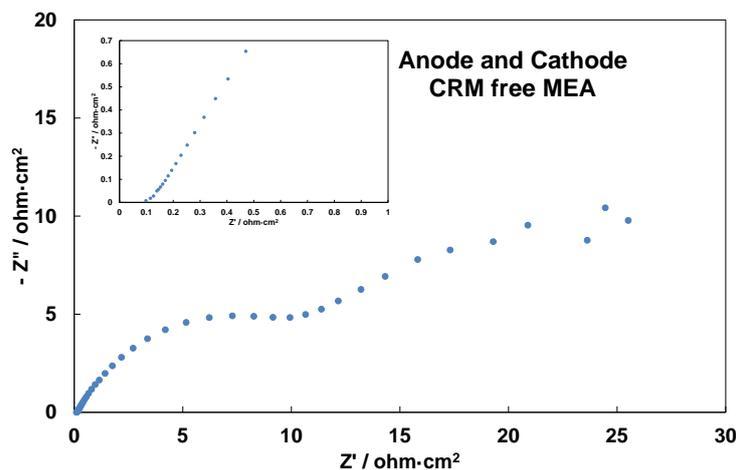


Figure 2.3 EIS for selected non-CRM anode and cathode electrocatalysts based MEA at 2 V and 80°C

Long term stability (about 2500 h) results, for the MEA totally based on CRM free-catalysts shows good stability (Fig. 3); however, cell voltage is much higher compared to conventional CRM based MEAs despite the significantly larger catalyst loadings.

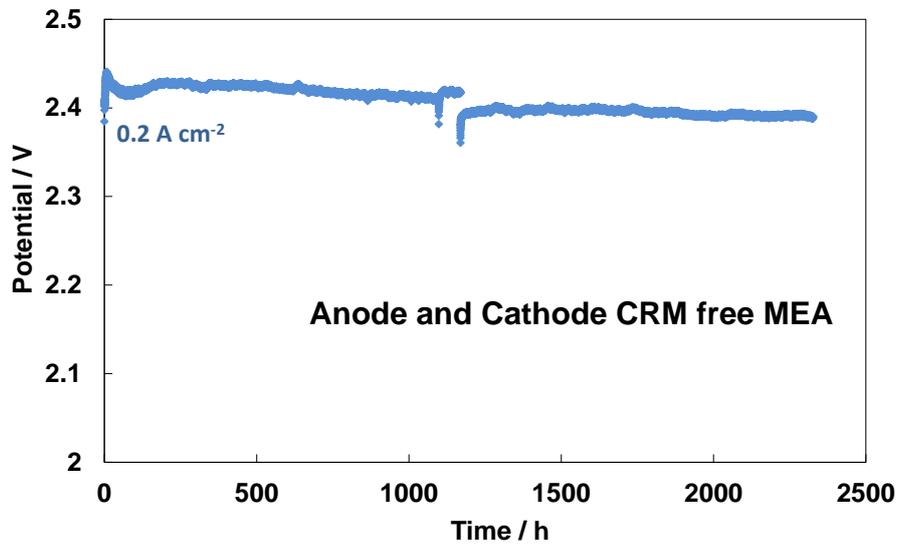


Figure 3. Chrono-potentiometric test at 0.2 A·cm⁻² and 80 °C for selected non-CRM anode and cathode electrocatalysts based MEA

In conclusion: The performance of non-CRM (according to 2017 EU classification) catalysts was significantly lower than the benchmarks IrOx/Pt catalysts despite the much larger catalyst loading (12 vs conventional 2-3 mg·cm⁻² for the anode and 1-2 vs conventional 0.2 mg·cm⁻² for the cathode). Despite the much lower voltage efficiency of non-CRM catalysts vs. conventional CRM catalysts a relatively good stability, after about 2500 h test, was observed.

Significant improvements are needed for non-CRM catalysts before these can become competitive with respect to low CRM loading electrocatalysts.

3 MEA performance assessment: *reduced CRM catalysts*

3.1 MEA preparation

The catalyst layers (CL) were made with a doctor-blade (Coatmaster 510, Erichsen GmbH & Co. KG) and using a spray-coating device (ExactaCoat, Sono-Tek). A typical dispersion for layer formation was processed by a dispersion device (Ultraturrax, IKA) and an ultrasonication finger (Sonopuls HD3400, Bandelin). For the doctor-blade, the dispersion was made with an appropriate mixture out of catalyst, Nafion dispersion (Ion Power), deionized water, 2-butanol (Merck), and 1-heptanol (Merck). Cathode 60% Pt/C (PK Catalyst) and for the anode IrO₂ (Alfa Aesar) were used as reference catalyst. Only for the cathode with a loading of 0.05 mg_{Pt} cm⁻² a 20% Pt/C (HISPEC3100) was used because it was not possible to form an appropriate layer with the 60% Pt/C catalyst. The cathode possessed a Nafion content of 20 wt% and the anode 14 wt.% inside the layer. The layers (4 cm², 17.64 cm², 25 cm²) were transferred onto the Nafion membrane (N117, Chemours) via hot-pressing at 130°C while using a joining time of 3 min at 40 kN. For the cell assembly, iridium sputtered Titanium fiber meshes (Bekipor® ST Titanium Grade 1) were used as porous transport layers on both sides, possessing a fiber diameter of 20 µm with a thickness of 1mm and a porosity of 56%.

The CL made by spray-coating was directly sprayed onto the Nafion membrane (N117) for IrO₂, while for Ir-ATO the CL was sprayed onto the decal sheet and the same hot-pressing parameters were used as for the doctor-blade derived samples. For the dispersion, a stable mixture out of deionized water and n-propanol (Merck) was used for both cathode and anode. The ratios between catalyst/Nafion and cell components were the same as described before.

3.2 MEA electrochemical characterization

Catalyst with reduced CRM content for the cathode

Platinum on molybdenum, designed in WP1, was selected as the material to replace the platinum on carbon catalyst, which is commonly used as a benchmark. The polarization curves obtained showed high overpotentials in the kinetic region and did not achieve comparable performance as the used Pt/C catalysts (Figure 4).

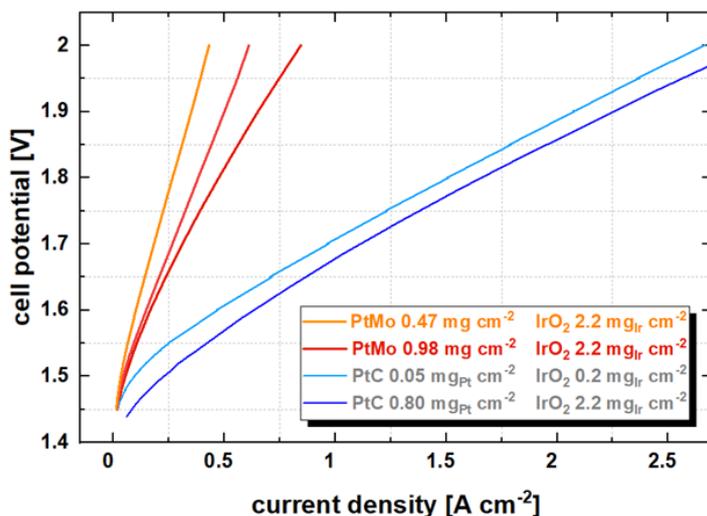


Figure 4. Recorded single-cell testing performance for different loaded Pt@Mo MEAs

The hysteresis of the forward and backward scan indicates that the electrode was not stable and its expansion is comparable at different loadings (Figure 5). Adjusting or stabilizing the electrode with more Nafion as a binder within the catalyst layer is not an option, as this would also increase the overpotential.

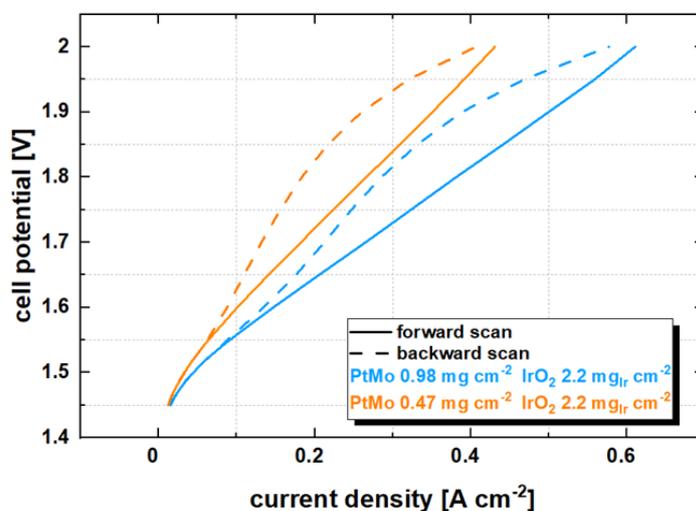


Figure 5. Occurring hysteresis for all Pt@Mo-based MEA indicating non-stable cathode

The blue traces were also present in this electrode after spray coating (Figure 6a). In addition, the necessary hydration step of the membrane after spraying showed that the electrode was very unstable in the presence of water (Figure 6b). The extent of material loss is not yet known, but this effect could be enhanced when this catalyst is operated at 80°C with constant water flow and applied current/potential in single cells. The reached performance at 2 V was 600 mA cm⁻², which is less than a third of the used Pt/C catalyst.

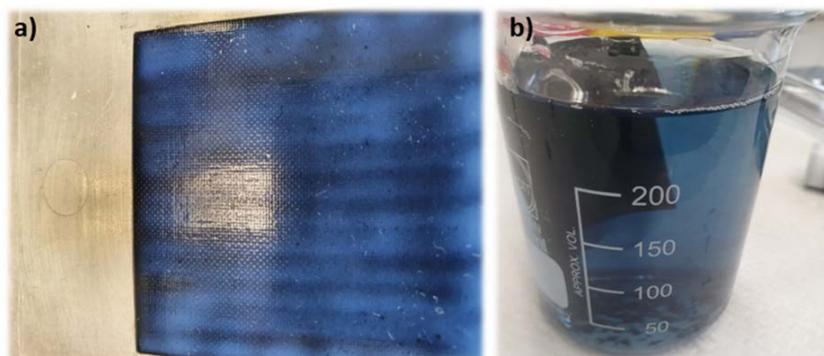


Figure 6. Backside of the membrane after spraying the catalysts as a layer on top (a) and impact of required hydration step on electrode stability (b)

Catalyst with reduced CRM content for the anode

Iridium on support material has been used to reduce the amount of iridium while maintaining or improving performance. Iridium on antimony tin oxide (ATO) is a successful material combination and was synthesized in WP1 with two different weight percentages of iridium (35 wt% & 50 wt %). The performance of Ir-ATO 35 wt% depended strongly on the loading applied (Figure 7). Low loadings of iridium, such as below $0.5 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ showed a strong hysteresis, even after the 10th polarization curve, and at the same time low performance at 2V ($< 1 \text{ A cm}^{-2}$). A loading of about $0.91 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ showed optimal performance, while further increasing the loading did not improve performance. Using instead Ir-ATO with an iridium content of 50 wt% improved the performance considerably. It was possible to achieve similar performance with a loading of $0.76 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ Ir-ATO 50 wt% as with the $2.2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ standard iridium loading. Reducing the loading to $0.36 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ also showed that the performance loss is comparatively small, especially in the kinetic region.

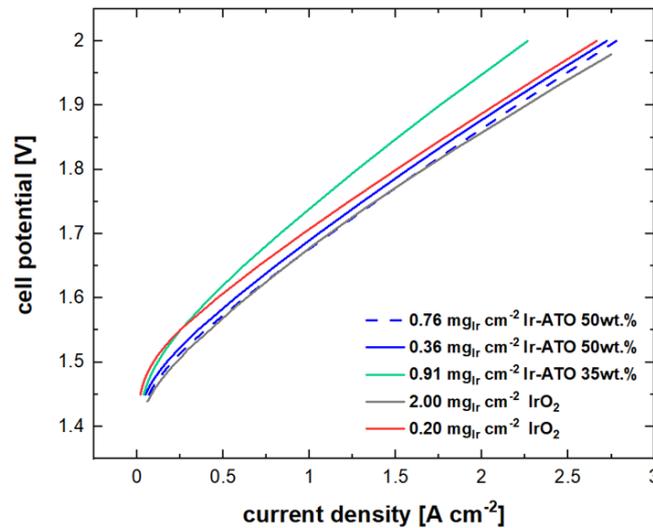


Figure 7. Single-cell testing results for different loaded Ir-ATO catalysts compared against benchmark catalysts

The stability of Ir-ATO 35 wt.% and 50 wt.% was tested at 2V for 250h (Figure 8) with an unusual dip after 60h which should be due to an issue with the test station. However, the polarization curves before and after testing showed similar behavior for Ir-ATO 35 wt.% and a slightly improved performance for Ir-ATO 50wt.% (Figure 8).

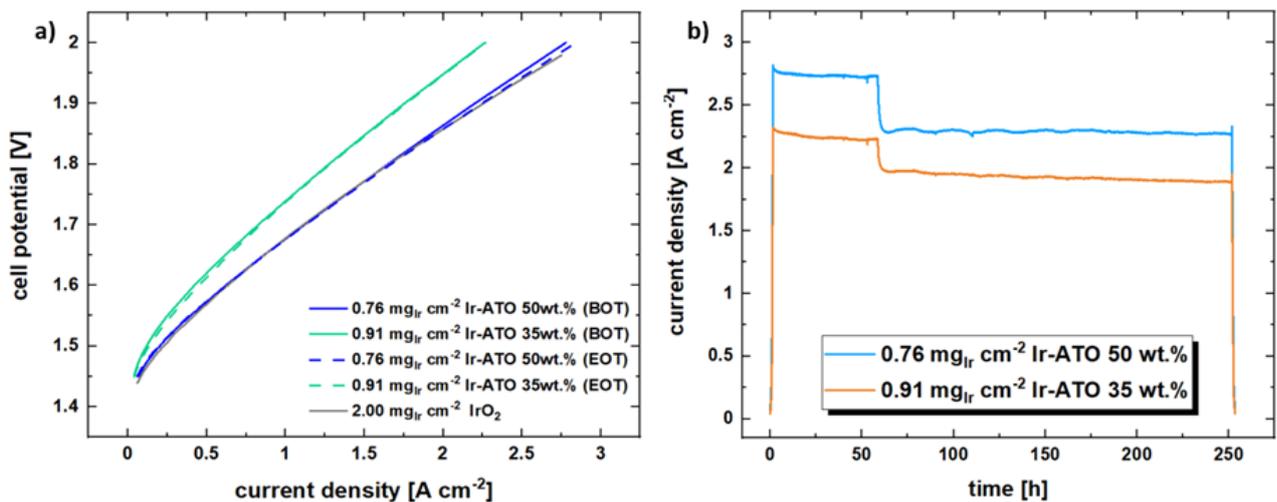


Figure 8. Results from durability study with (a) polarization curves at BOT & EOT as well as (b) monitored current density for 250h durability test at 2V with dip at 65h caused by the test station

The next step included a longer durability test for low-loaded MEA's and based on the NDP8003 membrane, developed within this project while using also the catalyst Ir-ATO 50wt.%. The relative current density decreased by 12% in the first 250h for loading of 0.36 mg_{Ir} cm⁻², while the 0.20 mg_{Ir}

cm⁻² loadings decreased only by 4% in the same period. This difference could be due to an issue with the PTL or single-cell. Instead, the relative current density decreased very strongly by 35% in case 0.19 mg_{Ir} cm⁻² loading was deposited on the thinner NDP8003 membrane, which needs to be investigated further. However, the change in relative current density was comparably small in the second 250h of operation. The high loading of 0.76 mg_{Ir} cm⁻² was also tested on this NDP8003 membrane at a current density of 3.97 A cm⁻² and showed a degradation rate of 46 μV h⁻¹ in the first 250h, determined from a fit in the linear region after 25h. However, during the second 250h, the loss rate was only 16 μV h⁻¹, which was close to the project target of 10 μV h⁻¹. The next steps must lead to an understanding of why the low loading decreased comparably faster on the thinner membrane NDP8003 than on the thicker N117 membrane.

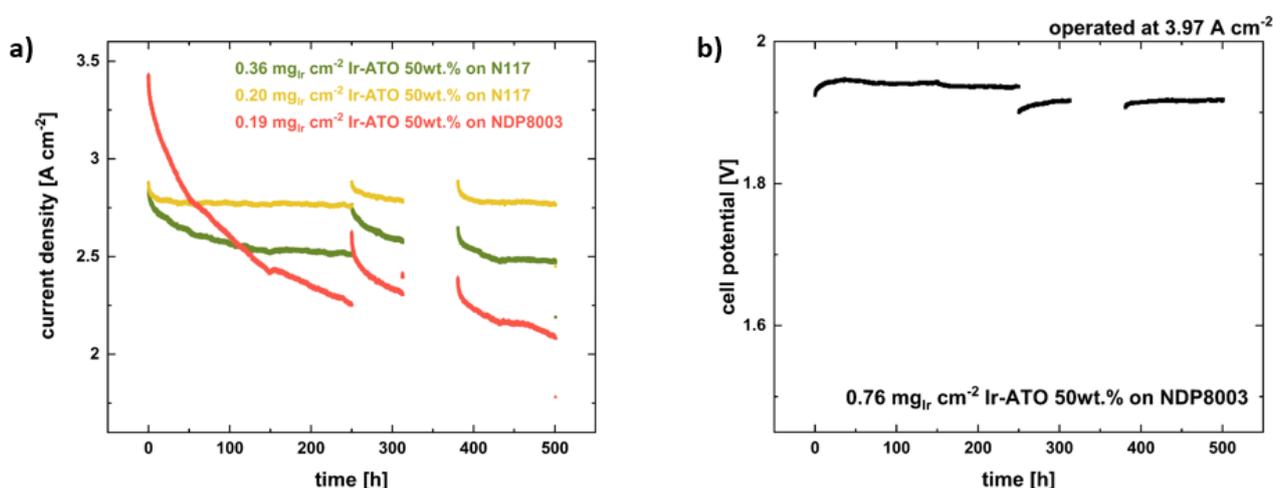


Figure 9. Testing the durability of low loadings with Ir-ATO 50 wt.% as anode catalyst deployed on N117 and NDP8003

Otherwise, it is proposed to reduce the Ir loading at the anode by using a catalyst based on Ir double perovskite with Ca (CSIC). The perovskite allows to reduce the loading of Ir in the anode side of the MEA to 0.4 mgcm⁻² and 0.2 mgcm⁻² with a performance of 1.81 V and 1.78 V respectively at a nominal current density of 2 Acm⁻² (Figure 10). It was possible to achieve similar performance with a loading of 0.2 mg_{Ir}cm⁻² as with the 1 mg_{Ir} cm⁻² standard iridium loading.

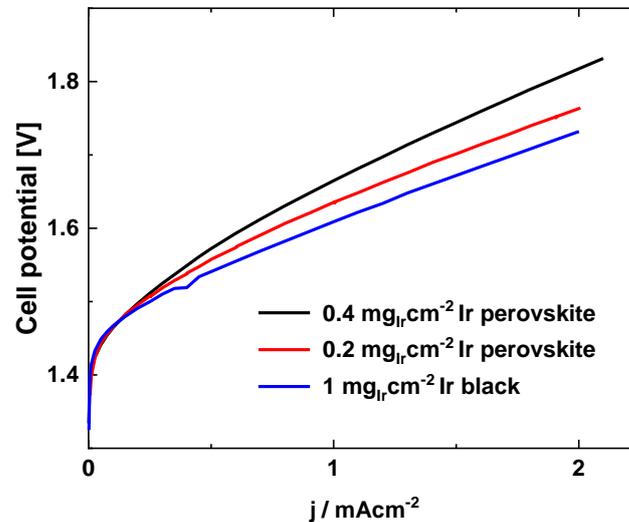


Figure 10. Single-cell testing results for different loaded Ir perovskite catalysts compared against benchmark catalysts

The stability of Ir perovskite with $0.4 \text{ mg}_{\text{Ir}}\text{cm}^{-1}$ as anode catalyst was tested for durability at a constant nominal load of 2 A cm^{-2} (Figure 11). The electrode shows an activation period during the first 50 h but afterwards the E_{cell} maintains practically constant for about 450 h proving that the electrocatalyst is stable in PEMWE conditions.

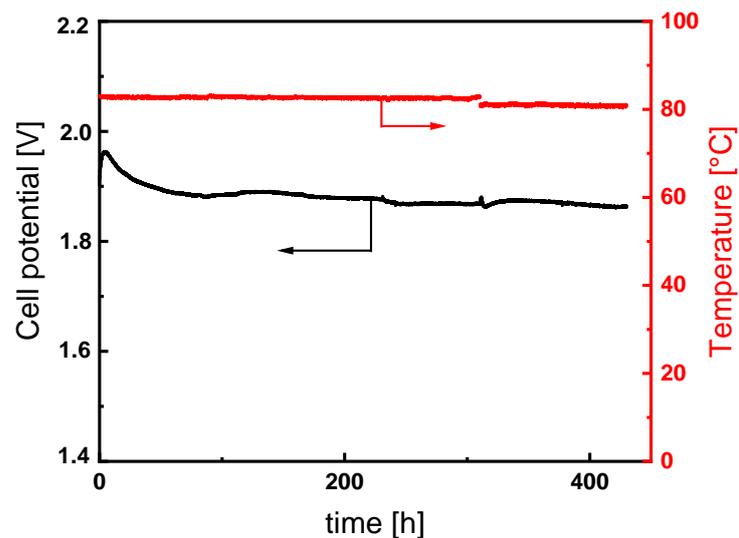


Figure 11. Testing durability of $0.4 \text{ mg}_{\text{Ir}}\text{cm}^{-1}$ with Ir perovskite as anode catalyst at a current density of 2 A cm^{-2} during 450 h

4 Cross-over measurement

The performance assessment of the different membranes was conducted by **FZJ** and **CNR-ITAE**. All MEAs tested were based on IrO₂, as anode, and Platinum, as cathode. The different membranes, supply by Chemours, were Nafion N117, ND8003 and NR212. The membranes information is reported in the table below:

Table1: membranes characteristics tested in single cell

	N117	ND8003	NR212	Unit
Thickness (50% RH)	183	80	50	μm
Areal Resistance (21°C, water soaked)	217	98	61	$m\Omega cm^2$
H2 Flux (90°C, 100%RH)	2.8	6.3	9.09	$10^{-14} mol/cm^2 s Pa$

At **FZJ** experimental for membrane performance evaluation and cross-over testing were conducted at an operation temperature of 80°C and a water flow rate of 50 mL min⁻¹ at ambient pressure. The protocol used for all MEAs was:

1. Activation
2. 10x Polarization curves (forward & backward)
3. cross-over measurement and durability test

In case of the durability test, the cross-over was monitored for 250h with a K1550 Gas Analyzer from HITECH Instruments. A different waiting times at different current density were used to receive a steady state signal from the gas sensor.

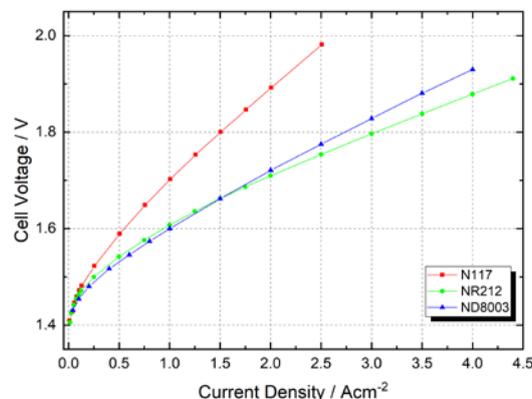


Figure 12. Polarization curves of different membranes tested at FZJ

Similar polarization curves were observed for the ND8003 and NR212 membranes based MEAs with thickness of 80 μm and 50 μm , respectively. Whereas for the N117 (thickness of 183 μm) based MEA is evident a decrease of performance with an overpotential over than 200 mV at 2.5 $\text{A}\cdot\text{cm}^{-2}$ (Fig. 12).

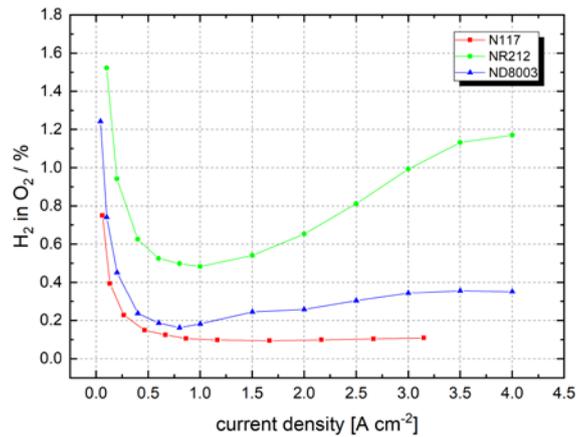


Figure 13. Cross-over measurement in single-cell assembly tested at FZJ

Monitoring over time the cross-over at high current density ($3.5\text{ A}\cdot\text{cm}^{-2}$) for the ND8003 based MEA is evident an increased from 0.4 % to 0.65% after the first 100, after that a constant cross-over of 0.65% after 100 hours of operation is showed (Fig. 14). Whereas for the N117 based MEA is observed nearly a constant cross-over of 0.45 % (Fig. 14).

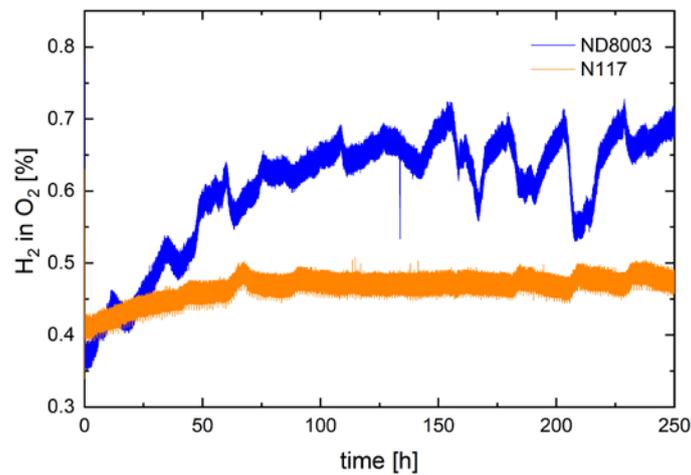


Figure 14. Cross-over monitored at $3.5\text{ A}\cdot\text{cm}^{-2}$ for 250h of operation using ND8003 and N117

At **CNR-ITAE** the electrochemical tests, polarization curves, Ac-impedance and H₂ permeation at the anode, were carried out in mode differential pressure (ambient pressure, 10 and 20 bar), with an operation temperature of 80°C and a water flow rate of 30 mL min⁻¹.

The quantitative analysis of hydrogen concentration was performed at constant current density (2 h under steady state for each applied current density) by a pressurised cell set-up in combination with a micro gas chromatograph (Varian Micro GC). The anodic gas stream was passed through a desiccator before being analysed.

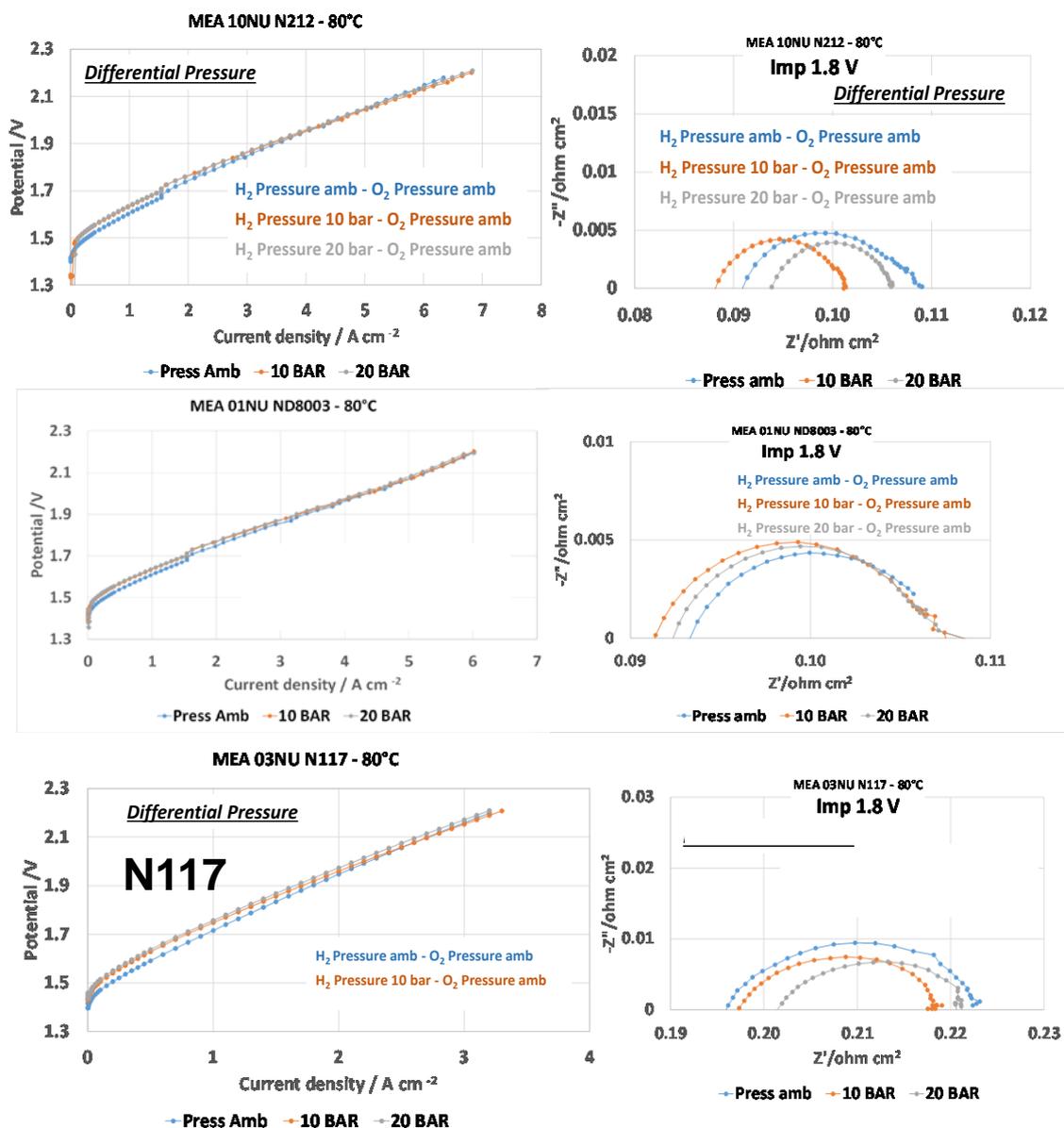


Figure 15. Polarization curves and ac-impedance of N212, ND8003 and N117 based MEAs tested at CNR-ITAE

From the polarization curves (Fig. 15) of the three different membranes with different thickness, obviously, we can observe a decrease of performance with an increase of the membrane thickness and a light decrease of performance at low current densities when there was an increase of pressure.

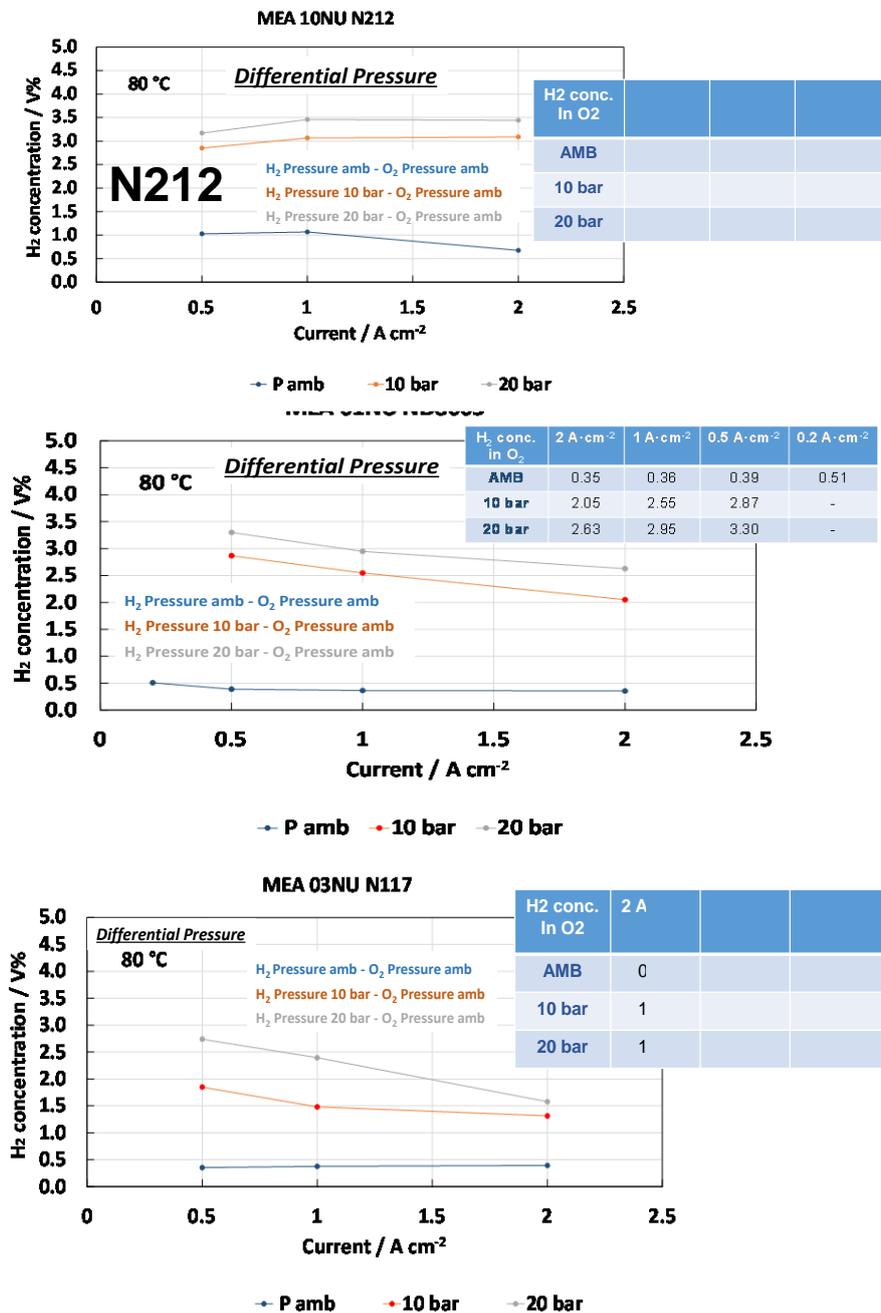


Figure 16. H₂ crossover in O₂ of N212, ND8003 and N117 based MEAs tested at CNR-ITAE

In conclusion: Cross-over measurements at ambient pressure showed that a permeation below 2% can be reached with all membranes tested. Only at very low current densities the cross-over was close to the threshold of 2.0 % H₂ in O₂. The membrane ND8003 were also tested in 250 hours long-term test at 3.5 A cm⁻² to monitor the cross-over on a proper time scale. The cross-over increased during the first 100 h of the measurement, but then the signal oscillated around a constant value of 0.65 % H₂ in O₂ until end of operation.

- All tested membranes (N117, ND8003, NR212) showed at ambient pressure a cross-over of < 2% at 0.5 A cm⁻² (FZJ)
- Durability test showed that the cross-over remained at 0.65 % H₂ in O₂ (FZJ)
- After applying high differential pressure, it was observed that the ND8003 membrane exceeded the 2 % H₂ in O₂ threshold at 0.5 A cm⁻² (CNR-ITAE)

Acknowledgement



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862253".