



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

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Executive Summary

Deliverable D2.2 "1st annual report on MEA performance assessment" will identify the main challenges that need to be overcome to achieve the desired goals of low PGM loading and non-PGM loading MEA architectures. First, the performance of the different loadings and catalysts must be determined. Maintaining the excellent performance of the PEM electrolyzers is imperative, as is their durability. Long-term testing with low and high PGM loadings will provide an assessment of the feasibility of using low-loading MEA architectures. This assessment will guide progress and identify the major challenges that need to be addressed in the project.

1 Introduction

The high cost of PEM electrolyzer components threatens the commercialization of PEMWE technology. In addition, recent studies have shown that the annual production rate of iridium limits the large-scale deployment of PEM electrolyzers. Extensive research is required to use fewer amounts of PGM or non-PGM catalysts while maintaining performance and durability. Achieving maximum performance requires understanding the relationship between MEA, fabrication, architecture, and catalysts used. When evaluating durability, the dependence between intermittent operation and degradation mechanism must be considered.

In this report, different MEA architectures and their current performance benchmarks are presented. The fabrication methods compared were doctor blade and spray coating using low PGM loadings.

For durability analysis, low and high PGM loaded MEA architectures were operated at 2V for 500h. MoS₂ was used as the first non-PGM catalyst cathode. The performance derived from different MoS₂ loadings was compared to the benchmark with low PGM loading MEA. An initial evaluation is made from these results, which are considered to derive strategies to improve MEA architectures in the future.

2 Initial approaches in the performance assessment of different MEA architectures

For the MEA performance assessment, single-cell testing were conducted with an ETS E100 electrolyzer test station (Greenlight Innovation). For each test, operation temperature of 80°C, and a water flow of 50 mL min⁻¹ was chosen under atmospheric pressure. After 2 hours of initial conditioning without applied current, the cell were operated for 30 minutes at a current density of 0.2 mA cm⁻². Subsequently, the current density was increased to 1.0 mA cm⁻² for another 30 minutes, followed by a continual operation step where the cell potential was set to 1.7 V for 8 hours. For the performance test, potentiostatic or galvanostatic testing were used and each measurement point held for 5 minutes until a maximum voltage of 2.0 V was reached. For each test a forward and backward scan were used.

The cell was disconnected from the test-station and connected to a potentiostat (HCP1005 Biologic) for potentiostatic electrochemical impedance spectroscopy (PEIS) measurements. The sinus amplitude was set to 10mV and a frequency range from 10kHz to 100mHz was chosen for each measurement.

2.1 Performance evaluation of MEA for different PGM loadings

2.1.1 MEA preparation

The catalyst layers used in this study were prepared using a doctor blade method (Coatmaster 510, Erichsen GmbH & Co. KG). A typical dispersion for the layer formation was processed by a dispersion device (Ultraturrax, IKA) and ultrasonic finger (Sonopuls HD3400, Bandelin). The dispersion was prepared using an appropriate mixture of catalyst, Nafion dispersion (Ion Power), deionized water, 2-butanol (Merck) and 1-heptanol (Merck). The catalyst used was 60% Pt/C for the cathode side (PK Catalyst) and IrO₂ (Alfa Aesar) for the anode side. For the low loading of 0.05 mg_{Pt} cm⁻² a 20% Pt/C (HISPEC3100) was used because a suitable layer could not be formed with the 60% Pt/C. The cathode possessed a Nafion content of 20 wt% and the anode 11 wt.% within the layer. The layers (4 cm²) were transferred to the Nafion membrane (N117, Chemours) by hot-pressing at 130°C using a joining time of 3 min at 40 kN.

Iridium sputtered titanium fiber meshes (Bekipor® ST Titanium Grade 1) on both sides were used as porous transport layers for cell assembly, with a fiber diameter of 20 µm at a thickness of 1mm and a porosity of 56%.

Assessing the possibility of low loadings requires comparison with high PGM loadings. Normally, high loadings are used to minimize the contribution to the electrical resistance of the cell, which is dominated by the membrane. The kinetic overpotential is expected to be less affected by lower loading, but more by its utilization, which becomes more difficult with lower layer thickness. Typically, a loading of $1 - 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ correlates with a layer thickness of $7 - 12 \text{ }\mu\text{m}$, whereas a loading of $0.5 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ correlates with a layer thickness in the range of about $2 \text{ }\mu\text{m}$. The lower layer thickness affects the contact efficiency between PTL and MEA, which could explain the trend of performance evaluation for different loading combinations in Figure 1.

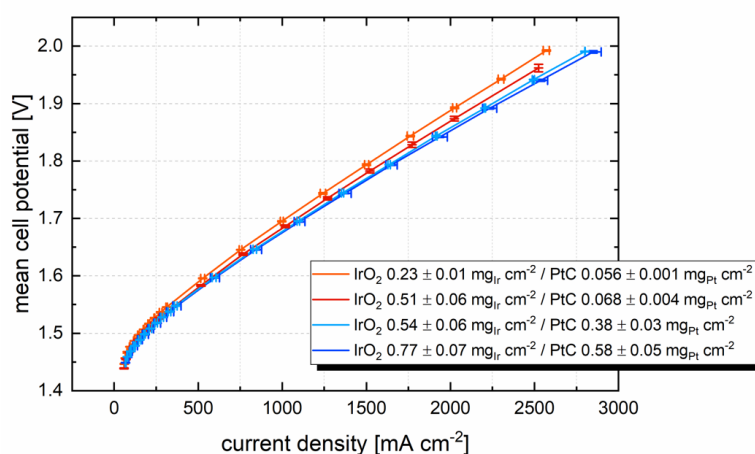


Figure 1. Screening the performance for different loadings made by the doctor-blade with a N117 membrane.

The polarization curves in Figure 1 show that the major performance loss occurs in the region where the electrical resistance of the cell is the main cause for performance losses and that losses in the kinetic region play a minor role. At 2 V, the most highly loaded MEA showed a current density of 2849 mA cm^{-2} , while the MEA with the lowest loading showed a performance of 2570 mA cm^{-2} , which is almost a 10% performance loss. Strategies to overcome this loss could be the deposition of layers with higher homogeneity or different PTL to improve the contact efficiency.

2.2 Benchmarking of low PGM loaded MEA for doctor-blade and spray-coating

The MEAs in this study were prepared using a spray-coating device (ExactaCoat, Sono-Tek), where the catalyst layer was sprayed directly onto the Nafion membrane (N117). A stable mixture of deionized water and n-propanol (Merck) was used for the dispersion for cathode and anode. The mixing

ratios between catalyst/Nafion and cell components were the same as described in chapter 2.1 for the performance evaluation of different loadings.

The doctor-blade is suitable for high loaded catalysts layers. However, it is limited in achieving very low and homogeneously loaded catalyst layers because of the need to apply non-uniform transfer foils whose thickness variation is often greater than the layer thickness itself for low loaded catalyst layers. Spray coating is not an option for high loadings on an industrial scale, due to the time required for spraying and the complexity of the catalyst layer architecture. Instead, the use of low loadings significantly reduces the spraying time, which could allow the use of spray coating of catalyst layers also for industrial scale. In Figure 2, the low loading performance benchmark produced with the doctor blade (grey curves) was compared to the best currently available performance derived from spray coating (orange curve) and to the existing spray coating performance benchmark (blue curve).

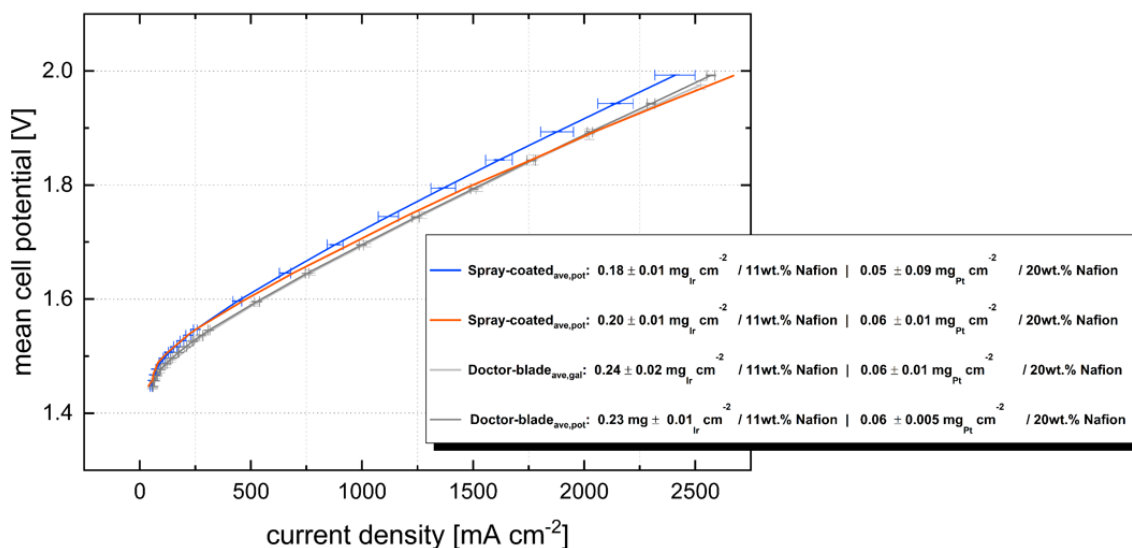


Figure 2. Comparison of low PGM loaded MEAs made by doctor-blade and spray-coating on N117 membrane.

Recognizable is the comparably higher standard deviation for the spray-coated samples and the lower performance in general. The next step is to perform a parameter study for the spray coating considering the adjustable parameters and the dispersions used. These results will be correlated with the layer properties such as thickness, density, and porosity as well as the layer homogeneity and electrochemical properties. The improved catalyst layer architecture will be tested on different membranes to maximize performance.

2.2.1 Impact of hydration on degradation of spray-coated membranes

During this study, another degradation mechanism was observed for the spray-coated MEA. Figure 3 presents two spray-coated MEA, brownish-colored MEA was untreated after spray coating (Figure 3a), and transparent MEA was hydrated (Figure 3b) by subsequently soaking the MEA in ultrapure water. The brownish coloration could indicate degradation of the membrane caused by the spray coating conditions, as the membranes are placed on a heated vacuum plate operated at a temperature of 80-90°C. After testing both MEA, higher crossover and lower performance were observed for the untreated one, while hydration protected the MEA from color changes and also reduced crossover. Hydration of the MEA could protect the membrane from degradation due to its water content, while the untreated and dry membrane is susceptible to degradation. However, the reason for this behavior needs to be analyzed in more detail in the future.

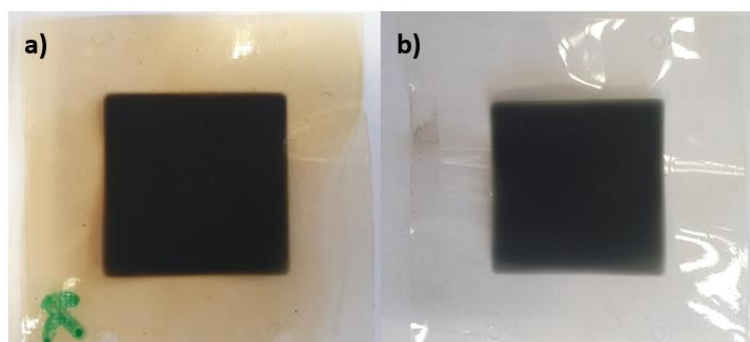


Figure 3. Degradation and protection of the MEA after spray-coating (a) untreated MEA after spray-coating with 90°C (b) hydrated and not degraded MEA after spray-coating at 90°C with subsequent hydration of the MEA.

2.3 Assessment of the durability and comparison of low and high loaded MEAs

Another critical requirement for making low-loaded MEA is maintaining durability. For this reason, two MEA with high and low PGM loading were tested for 500h at 2V using the same measurement protocol and membrane (N117). In Figure 4a, the straight line denotes the polarization curve at the beginning of the test (BOT), while the dashed line refers to the polarization curve after the 500h test (EOT). The polarization curve at the BOT and EOT differed greatly for the low loading MEA, while the high loading showed no loss in performance. Analysis of the high-frequency resistance (HFR) and IR- correction (Figure 4b) showed that the resistance increased

sharply, which is likely due to the layer passivation and catalyst dissolution. A more detailed post-mortem characterization should help to derive strategies against the strong performance degradation.

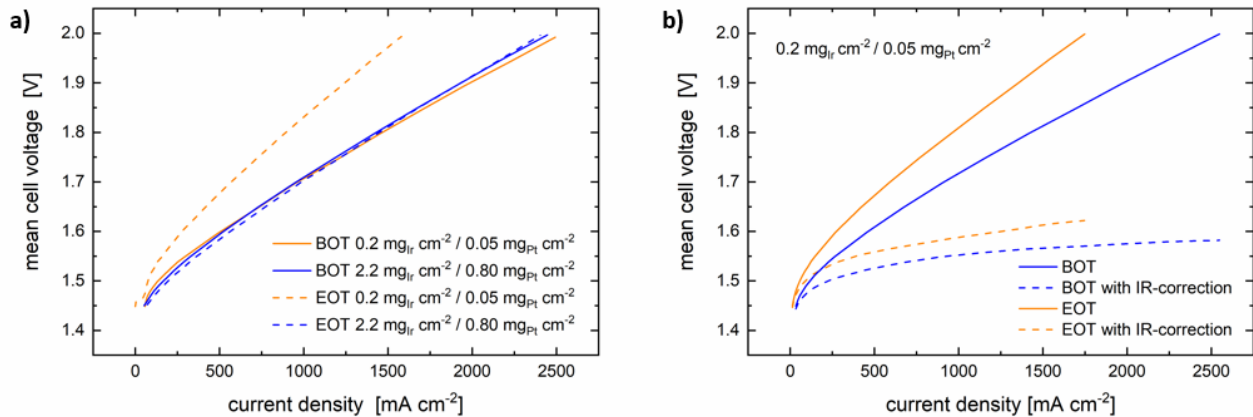


Figure 4. Polarization curves obtained before and after the 500 h testing (a) for high loading (b) IR-correction for the low loading before and after testing.

The monitoring of the 500h test is shown in Figure 5a for the low loading and in Figure 5b for the high loading. For both loadings, the water-resistance increased during the test at the anode, while the water resistance remained unchanged at the cathode side. The increasing water resistance correlates with the dissolving species and its slope correlates well with the decreasing performance curve. The 500h tests showed that the main problem with using low PGM loaded MEA results from durability and not from the performance loss.

The interpretation of the cross-over is limited in this study because two different cell sizes were used. For the low loading (Figure 5a) a cell size of 4 cm² was used, while a 25 cm² cell size was used for the high loading (Figure 5b). The cell size of 4 cm² produced low gas streams for the sensor to accurately determine the gas cross-over. It is expected that the cross-over is highly dependent on the membrane thickness and that the cross-over in Figure 5b is more accurate, as this cell size produces significant amounts of gas during the measurement.

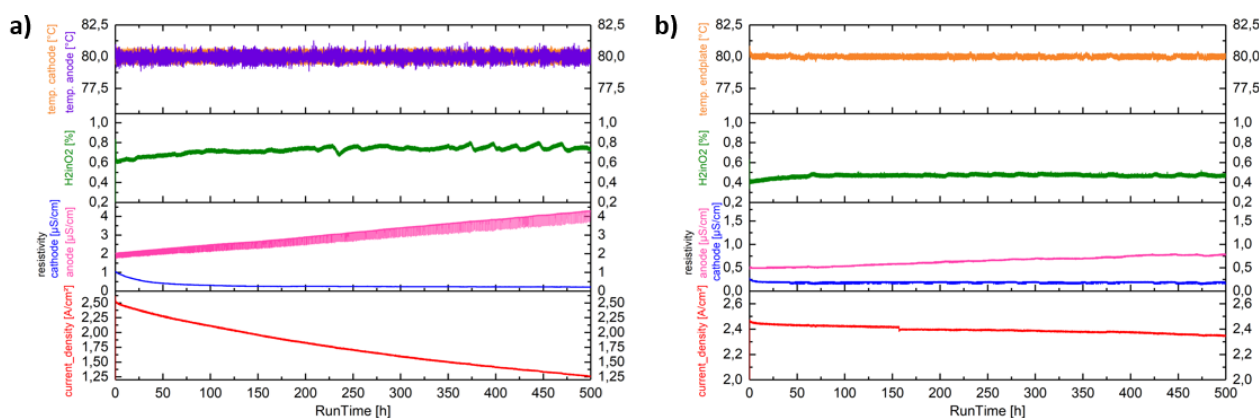


Figure 5. Monitoring of the 500 h testing for the (a) low loading and (b) high loading.

2.4 Performance analysis of novel catalysts for the Anode $\text{Sr}_x\text{CaIrO}_x$ perovskite

In search of novel OER catalysts, CSIC has prepared mixed oxides with reduced Ir content (see D1.2). The novel phases are double perovskites with the formula $\text{Sr}_x\text{CaIrO}_x$. DLR developed some MEAS using $\text{Sr}_x\text{CaIrO}_x$ as anode catalyst and performed the performance analysis.

The results reveal any mass transport limitation. Comparing the performance of the cell with the highest performances reported so far by other authors from well-known R&D institutes in the field of electrolysis, the new catalyst is able to compete.² Furthermore, if we consider the performance of commercial PEMWEs from manufacturers such as Siemens, Proton Onsite and Hydrogenics, these can be matched by the newly developed $\text{Sr}_2\text{CaIrO}_6$ catalyst with the same potential in comparison. Further information can be found in D1.2.

2.5 Performance analysis of non-PGM catalysts for the cathode

Non-PGM materials provide a cost-effective alternative to replace PGM catalysts. MoS_2 was used as the HER catalysts to replace Pt in the cathode side. The ink made from MoS_2 contains n-propanol and water at less than 0.5% by weight, as this is most effective for stabilization, and was then sonicated in ice bath for at least 30 minutes. The MoS_2 ink was sprayed directly onto the Nafion N117 membrane to verify the required loading and performance of this PGM-free catalyst. Figure 6 shows that the performance of MEA with MoS_2 (anode: $2.2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$) cannot

compete with the performance of MEA with low PGM loading ($0.2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ & $0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) and also increasing the loading of MoS_2 resulted in the same performance.

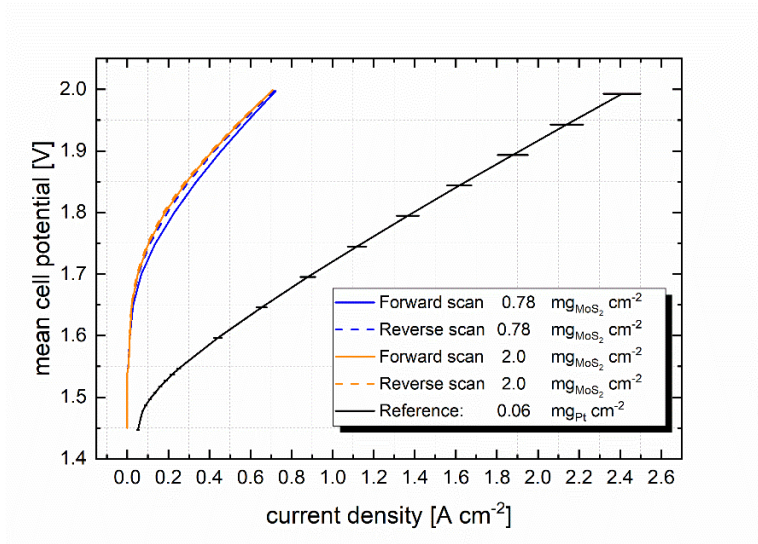


Figure 6. Performance screening for the MoS_2 catalyst with two different loadings on a Nafion N117 membrane.

Comparison of our results (Figure 7a) with the literature (Figure 7b) shows similar performance. The performance from our study showed a current density of 0.17 A cm^{-2} at 1.8 V while the MEA presented by Corrales-Sánchez et al. (2014) obtained a current density of 0.18 A cm^{-2} at 1.8 V . [1]

They obtained a constant current density of about 0.35 A cm^{-2} at 2 V , after a continuous operation of 15 h . Our study obtained a current density of 0.71 A cm^{-2} after 10 polarization curves (forward & reverse).

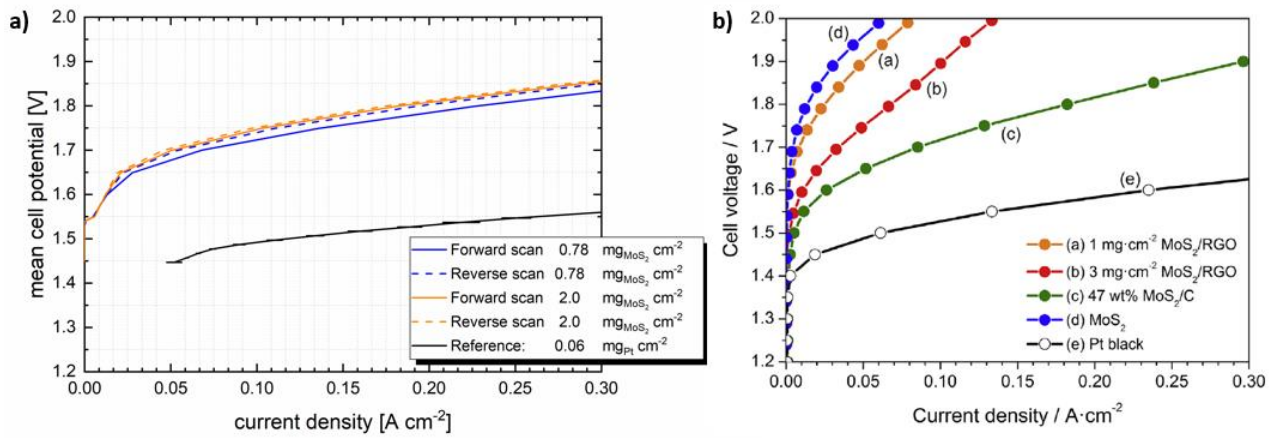


Figure 7. Comparison of the results of this study with results from Corrales-Sánchez et al. (2014) indicating a similar trend of performance.

2.6 Performance analysis of non-PGM catalysts for the Anode (CNR-ITAE)

An Ag/Ti-suboxide was tested as non CRM (according to 2017 EU classification) anode electrocatalyst in a single cell of 5 cm². Composition and characteristics of the MEA based on Ag/Ti-suboxide are reported in Table 1.

Table 1 – MEA based on non CRM (according to 2017 EU classification) anode electrocatalyst: composition and characteristic

Anode Catalyst	Anode Catalyst loading/mg/cm (Ti mesh substrate)	Membrane	Cathode Catalyst	Cathode Catalyst loading/mg/cm ² (GDL HT carbon)	V @ 0.6 A cm ⁻² (IR-free) (Single cell Target 0.6 - 1 Acm ⁻² @ 1.8V vs.IR free)	V @ 1 A cm ⁻² (IR-free) (Single cell Target 0.6 - 1 Acm ⁻² @ 1.8V vs.IR free)	Rs / mΩ·cm ² (1.8V)
Ag/Ti-suboxide (20:80 % _{at})	12.8 (33 % Nafion)	115	40% Pt/C	0.5 (33 % Nafion)	2.01	2.09	137

2.6.1 MEA preparation

A slurry composed of 67 wt.% Ag/Ti-suboxide catalyst and 33 wt. % Nafion ionomer (5 wt.% Ion Power solution) in deionized water and absolute ethanol alcohol (Carlo Erba) was prepared by mixing under ultrasonication. The slurry was directly deposited by using a spray coating technique

onto a Titanium fiber mesh, 300 μm thick, which has a porosity of about 70 % porosity. A benchmark 30% Pt/Vulcan catalyst was used for the H_2 evolution. The cathode catalyst 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 ionomer content in the cathode layer after drying was 33 wt. %. A Nafion 115 membrane was used for the single cell test. The MEA, with 5 cm^2 geometrical area, were prepared by a hot-pressing procedure by lamination at $130 \text{ }^\circ\text{C}$ for 1.5 min.

2.6.2 Electrochemical characterization

The single cell performance was evaluated at $80 \text{ }^\circ\text{C}$ and under atmospheric pressure. Deionized water was preheated to the same cell temperature and supplied to the anode compartment by a pump at a flow rate of $4 \text{ ml}\cdot\text{min}^{-1}$. 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 0.01 V r.m.s. The series resistance was determined from the high frequency intercept on the real axis in the Nyquist plot.

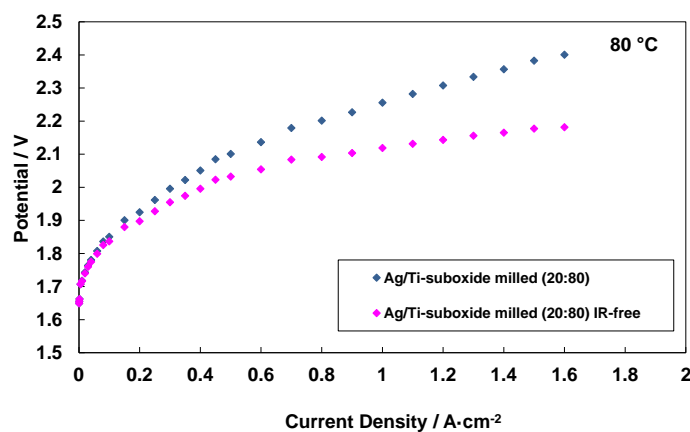


Figure 8. IV polarization curves for Ag/Ti-suboxide anode electrocatalyst based MEA.

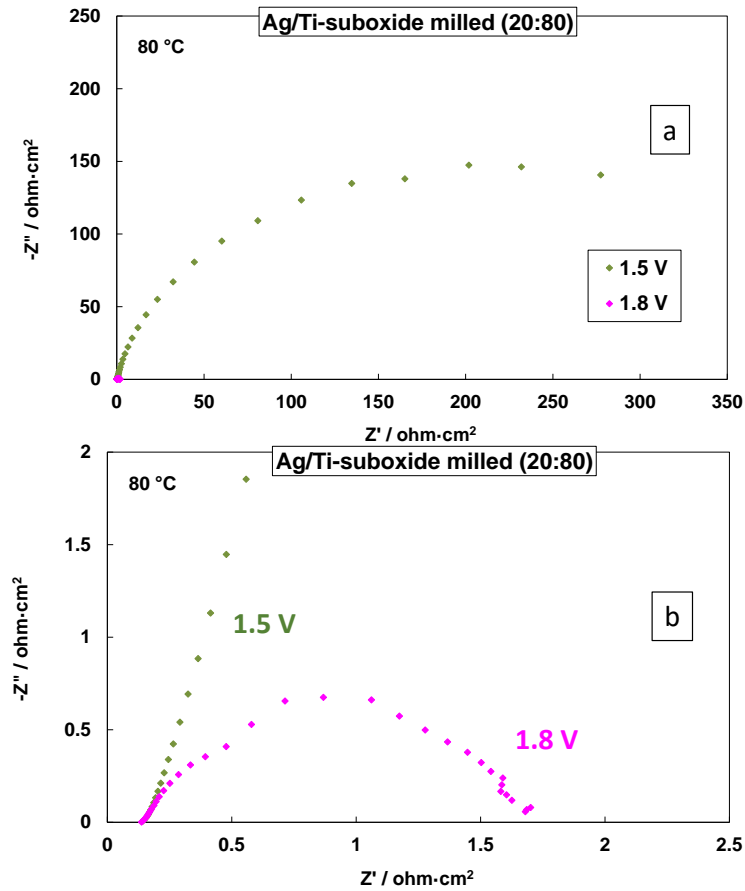


Figure 9. EIS for Ag/Ti-suboxide anode electrocatalyst based MEA at 1.5 V and 1.8 V (a), magnification on the EIS (b).

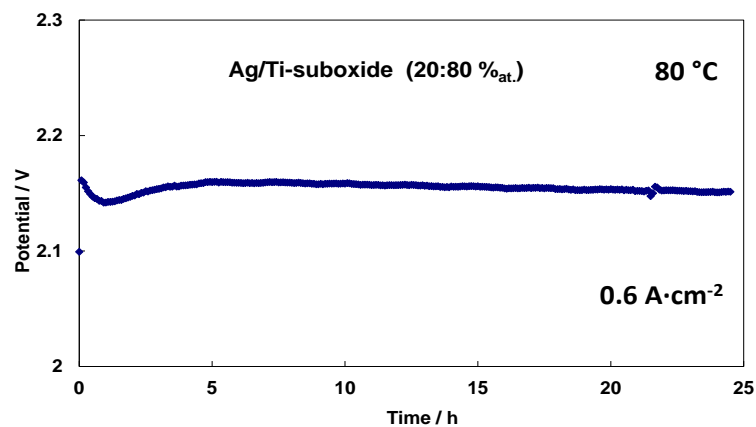


Figure 10. Chrono-potentiometric test at 0.6 A·cm⁻² and 80 °C for 24 h for the Ag/Ti-suboxide catalyst based MEA

IR-free single cell performance (Fig. 8) was 200 mV far from the non PGM project target (2 V vs. 1.8 V target at $0.6 \text{ A}\cdot\text{cm}^{-2}$). The performance of non CRM (according to 2017 EU classification) anode electrocatalysts was significantly lower than the benchmark IrOx catalyst despite the much larger catalyst loading (12 vs conventional 2-3 $\text{mg}\cdot\text{cm}^{-2}$).

3 Summary

The first report evaluating novel MEA architectures for the acceleration of the market, identified several issues to consider. For the low-loaded MEA, performance decreased by about 10% compared to the high-loaded MEA. Moreover, maintaining performance seems to be more accessible than durability. It is crucial to derive strategies to improve the durability of the low-loaded MEA to eventually achieve the desired goals in PROMET-H2. $\text{Sr}_2\text{CaIrO}_6$ perovskite was tested as anode for PEMWE. There is no evidence of mass transport limitation in electrochemical performance both polarization curve neither EIS. This catalyst has demonstrated to be a competitive candidate obtaining similar performance to those obtained in state of art (more bibliography information in D1.2). MoS_2 as non PGM cathode was tested with two different loadings that did not differ from each other. Ag/Ti-suboxide was tested as non PGM anode; significant improvements are needed for non PGM anode catalysts before these can become competitive with respect to low PGM loading anode electrocatalysts. Further progress needs to be made for both PGM and non PGM catalysts development and MEA implementation.

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