Deliverable Report

Testing protocols for characterization of anodes in PEM water electrolysis (D.1.1)

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DC-PEM Project
*Development of a **C**ost-effective anode for **PEM** water electrolysis*

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Abbreviation list[1]

BET - Brunauer-Emmett-Teller Method

BPP – bipolar plate

CE – counter electrode

CL – catalyst layer

CV – cyclic voltammetry

DOE – U.S. Department of Energy

ECSA – electrochemical surface area

EDX - Energy dispersive X-ray spectroscopy

EIS – electrochemical impedance spectroscopy

EoL – End of Life

EU – European Union

FCH2JU - Fuel Cells and Hydrogen 2 Joint Undertaking

GDL – gas diffusion layer

HER – hydrogen evolution reaction

JRC – Joint Research Center

LSV – linear sweep voltammetry

MEA – membrane electrode assembly

MPL – micro-porous layer

OCP – open circuit potential

OER – oxygen evolution reaction

PEMEL – proton exchange membrane electrolysis

PEMWE – proton exchange membrane water electrolyzer

PTL – porous transport layer

RE – reference electrode

SEM -scanning electron microscopy

SHE – standard hydrogen electrode

TEM – Transmission Electron Microscopy

WE – working electrode

XRD - X-ray diffraction

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[1] *According to EU harmonised terminology for hydrogen generated by electrolysis, Malkow, T., Pilenga, A., Blagoeva, D., 2021, Joint Research Center*

Summary

The deliverable 1.1. *Testing protocols for the characterization of anodes in PEM water electrolysis* as part of the WP 1, aims to define the testing procedure approached within the DC-PEM project, regarding the methodology used to characterize the performance of the newly developed anodes for PEMWE. The testing protocols, as specified in the D1.1. constitute an internal guide for the activities and tasks from WP 2, WP 4, and WP 6, described in the project proposal. The testing specifications correspond to the state-of-the-art and the recommendations of the advisory board and partners' testing practices, considering also the FCH JU harmonized specified guidelines and protocols, as well as the DOE specifications. The experiments carried out according to the defined protocols aim to enable proper planning and to indicate the achievements of the project objectives and milestones. The content of the deliverable 1.1 consists of:

- A brief state-of-the-art in the field of PEMWE;
- A testing protocol for corrosion resistance and stability assessment of the PTL/CL;
- A testing protocol for the anode catalytic activity and stability in a three-electrode cell configuration;
- A testing protocol for anode operation performance in a half-cell configuration (durability and activity towards oxygen evolution reaction);
- A testing protocol for anode operation performance in a full-cell (in-situ) configuration.

Table 1. Detailed description of the work package

WP number	1	Lead beneficiary	UPT	Start month	1	End month	6
WP title		Technical requirements PEM					
Participants		HSMW	IFAM		UCTP	LeanCat	
Objectives		Definition of the characterization methods and determination of the specifications with requirements and parameter set of the newly developed electrodes, considering the state of the art.					
Type of activities		Close interaction with the advisory board and literature research.					
Description of content		**Task 1.1. State-of-the-art PEM water electrolysis (lead: UPT)** Creation of an overview of the current PEM electrolyzers and their manufacturing costs and manufacturing technologies. Definition of technical test regulations for characterization of commercial benchmark electrodes. Estimation of the production costs for selected heights, considering deduction of the specification sheet with technical, environmental, and economical requirements for the new cost-efficient anode. **Task 1.2. Definition of requirements (lead: UPT)** In consultation with the advisory board, the current developments in the industry are evaluated and the following requirements are formulated.					
Milestones		**M 1.1.** Technical requirements for the cost-efficient anodes are established					
Expected results and deliverables		D1.1: Mandatory test protocols that correspond to the state of the art and the recommendations of the advisory board (M1.1. - all partners).					

Task 1.1. State-of-the-art PEM water electrolysis

To achieve climate neutrality, the European Green Deal has targeted a gradual reduction of greenhouse gas emissions by 2050 up to 80–95%, compared to the levels reported in 1990 [1]. The transition to this ultimate climate goal is sustained by several policy initiatives covering all relevant sectors like the environment, energy, transport, industry, and agriculture. Among the Green Deal projects, the 'Fit for 55' package, which is currently in progress at the European Council aims to align the EU laws with the climate goals and to establish new important rules to reduce emissions by at least 55% by 2030 [2]. This proximal goal has emerged in great interest for alternative carbon-free energy sources. The main pillars of global decarbonization are renewables, hydrogen, and electrification correlated with better energy efficiency, as presented in Figure 1 [3].
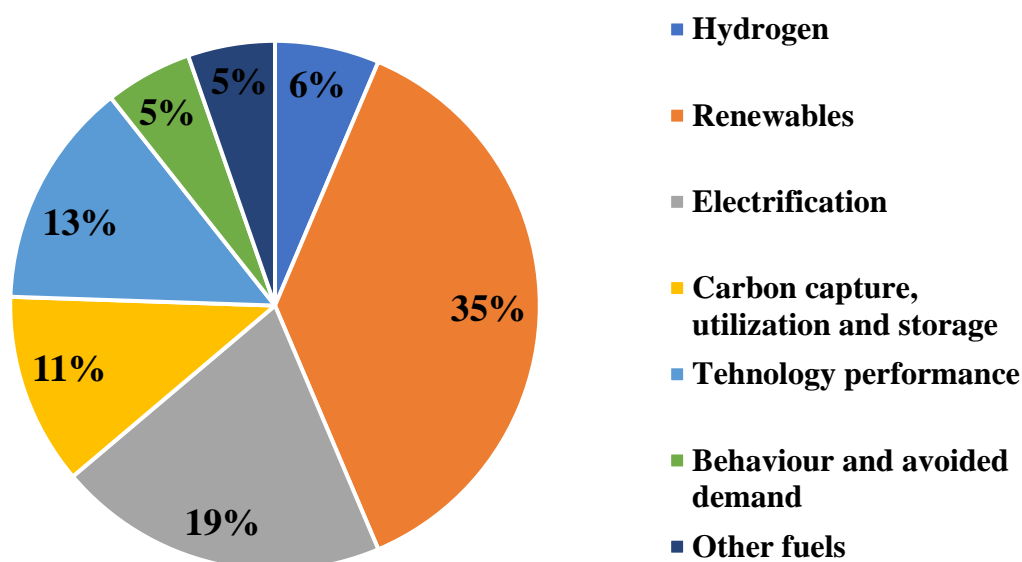
Figure 1. Emission reduction by mitigation measures [3]

For the moment, the most widely used strategy to step towards a zero-emission society is the incorporation of significant renewable energy sources like wind and solar power into the global economy. This measure primarily supports the decarbonization policy but also provides a sound plan for achieving energy-independent sectors and uniform distribution of energy. Due to the intermittent nature of such energy sources correlated with the limited electric storage capacity, the use of hydrogen as an energy carrier is considered to be crucial in struggling against climate change [4]. Hydrogen is currently used in various applications like power systems, transportation, hydrocarbon, and ammonia production, as well as metallurgical industries. Hydrogen is specifically critical for reducing emissions in the hard-to-decarbonize sectors, where direct electrification is difficult to implement, for example, heavy industry (steel manufacturing and chemical production), heavy-duty road transport, shipping, and aviation. The world's first pilot project, HYBRIT, for producing fossil-free steel using low-carbon hydrogen started to successfully operate in 2021 in Sweden. Another important project which

aims to produce ammonia based on green hydrogen is currently in progress in Spain. Furthermore, the global hydrogen demand is planned to increase from 70 million tonnes in 2019 to 120 million tonnes by 2024. There are various renewable sources used in hydrogen production, however, the inconsistency of these resources is the major challenge in the transition towards a real hydrogen economy. At this time, less than 1% of EU hydrogen is produced using environmentally friendly technologies, such as electrolysis (green hydrogen), while the majority (95%) is produced using the carbon-related processes of steam methane reforming under harsh conditions, which are restrained by complex operations correlated with high carbon dioxide emissions [5], and to a lesser extent, auto-thermal reforming [6].

Electrochemical water splitting is an effective and clean alternative to produce high-purity hydrogen. When coupled with a renewable source of energy, water electrolysis enables the production of decarbonized hydrogen at low temperatures (< 100°C). During the electrochemical water splitting, hydrogen evolution reaction (HER) takes place at the cathode, and oxygen evolution reaction (OER) at the anode. The occurrence of both reactions theoretically requires a voltage of 1.23 V. However, in practice, a larger voltage of about 1.8 - 2.0 V is necessary due to the overpotentials on both the cathode and anode. Hence, different types of electrocatalysts have been developed and tested to reduce the overpotentials for both HER and OER [5]. Combining electrolysis-generated hydrogen with proper storage in underground porous media is regarded as an alternative for taking advantage of intermittent energy generation from renewable sources [6]. However, this key technology for clean hydrogen production currently presents several vulnerabilities, as a recent report of the U.S. Department of Energy [7] has lately described:

- Immature technology that is not currently cost-competitive for both electrolytic hydrogen production and utilization;
- Insufficient infrastructure to support hydrogen markets at their potential;
- Availability of key raw materials involved in the production process;
- Growth requirements of manufacturing capacity and supply chains.

Several electrolysis and fuel cell technologies are currently available or under development. Electrolyzers that exclusively use electricity are referred to as low-temperature electrolyzers due to their low-temperature operation (lower than the boiling point of water). Low-temperature electrolyzer technologies encompass alkaline electrolyzers, proton exchange membrane water electrolyzers (PEMWE), and anion exchange membrane water electrolyzers. Proton exchange membrane electrolysis (PEMEL) is a less mature technology compared to alkaline electrolysis but exhibits great potential for cost reductions and large-scale exploitation due to higher production rates. Other advantages of PEMEL compared to alkaline systems are the high current densities (> 2 A cm^{-2}), high gas purity, low gas cross-over, and the possibility to operate stacks at high pressure (up to 350 bars) and wide operating temperatures (20 - 80°C) [8]. Moreover, PEMWE can ramp operation up and down at faster rates than traditional alkaline electrolyzers making them suitable for directly coupling to variable renewable energy sources such as wind or solar [7].

A PEMEL stack consists of repeating cells that are electrically connected in series and reactant water/product gas connected in parallel. Thick metal plates at both ends are included to structurally hold the cells inside the stack. At the core of each cell (Figure 2) is a polymer

membrane with cathode and anode catalyst layers (CL) situated on both sides of the membrane to form what is called membrane electrode assembly (MEA). The function of the catalyst is to increase the electrochemical reaction rate, in this case, the water splitting, by reducing the activation energy. Typical CL materials are iridium and ruthenium oxides for the anode and platinum for the cathode. When such precious materials are involved as catalysts, it is important to maximize their use by increasing the electrochemical surface area (ECSA). For this reason, some porous support structures like porous titanium (Ti) or Magnéli phase, are used for the anode. Carbon fibers are suitable only for the cathode due to their poor corrosion resistance in the anodic environment. The porous transport layer (PTL) is therefore, a structural element, consisting of a layer that assures support for the catalyst and enhances water diffusion and water-splitting reaction on the surface of the membrane in the electrolysis cells. The effectiveness of the PTL, especially at high current densities, may be improved by an additional layer deposited on the electrode side, also called the micro-porous layer (MPL). The MPL improves the performance, durability, and stability of the electrode, reduces the interfacial contact resistance, and protects the membrane from being penetrated by the PTL. Furthermore, PTL can be subjected to electrochemical degradation due to the combination of factors, such as temperature changes and the acidic environment, combined with mechanical degradation due to the compression effects. Also, when differential pressures are applied, the PTL needs to provide mechanical support for the membrane [9].

The electrolyte (membrane) is made of water-saturated proton-conducting perfluorosulfonic polymers, such as Nafion®, Aquivion® and Fumapem® commercially available membranes. The environment that surrounds the MEA is acidic, and therefore special requirements are demanded for the materials used as catalysts as well as for the structural elements that should be chemically stable and corrosion-resistant. Bipolar plates (BPP) as the name suggests, have a cathodic side and an anodic side. Their main function is to electrically connect the cells in a PEMWE stack, to separate the cells, and to facilitate the transport of water, hydrogen, and oxygen inside the stack [10].
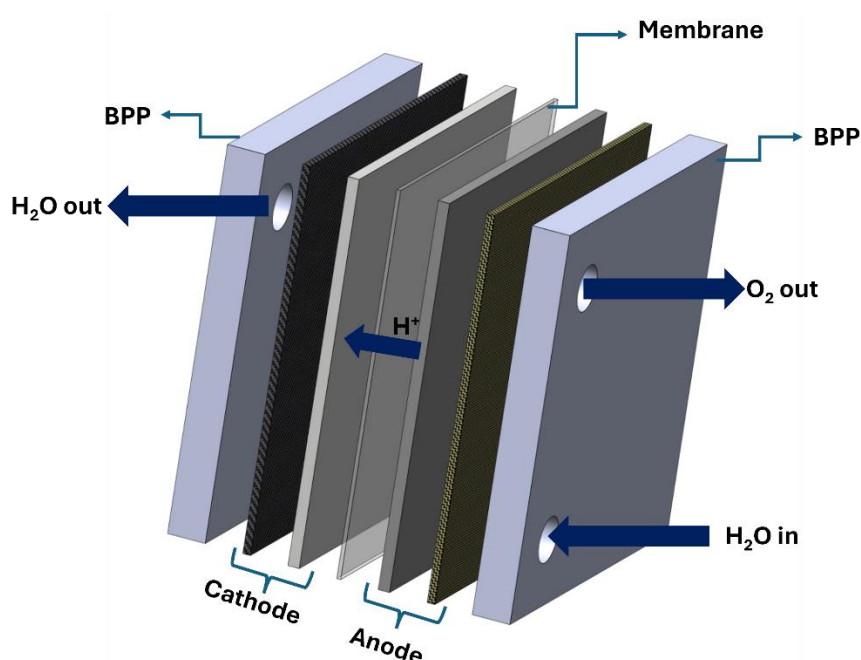
Figure 2. Key components in a PEMEL single-cell

On the anode side, the state-of-the-art material for BPP is titanium, due to the higher corrosion resistance under the specific operating conditions of PEMEL (high electrochemical potential, acidic, and oxidizing environment) compared to other materials [8]. The overall working conditions of a PEMWE are presented in Table 1.

Table 2. PEMWE overall working conditions [11]

PEMWE overall working conditions	
Charge carrier	H^+
Reactant	Liquid water
Electrolyte	Proton exchange membrane
Anode	IrO_2; IrO_2/Ti_4O_7; $Ir_xRu_yTa_zO_2$, Ir black
Cathode	Pt/C
Current density	$0.2 - 8.0$ A cm^{-2}
Operating temperature	$20 - 80$ °C
Pressure H$_2$ out	$10 - 30 \cdot 10^5$ Pa
Anode reaction	O_2 evolution reaction (OER): $2\,H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(aq.) + 4\,e^-$
Cathode reaction	H_2 evolution reaction (HER): $4H^+\,(aq.) + 4e^- \rightarrow 2H_2\,(g)$

Consequently, the PTL, especially the PTL anode, the CL along with the membrane, and the BPP are the primary cost contributors in the basic design of a PEMWE. Electrolytic hydrogen production relies mainly on expensive materials like iridium, platinum, gold, or titanium, which are mainly responsible for the low attractiveness of such technology. The actual costs of this technology are nevertheless very high, estimated at over 1000 €/kW, while over 30% are costs related to stack fabrication, according to the bar chart presented in Figure 3.

Figure 3. Detailed PEMEL stack costs

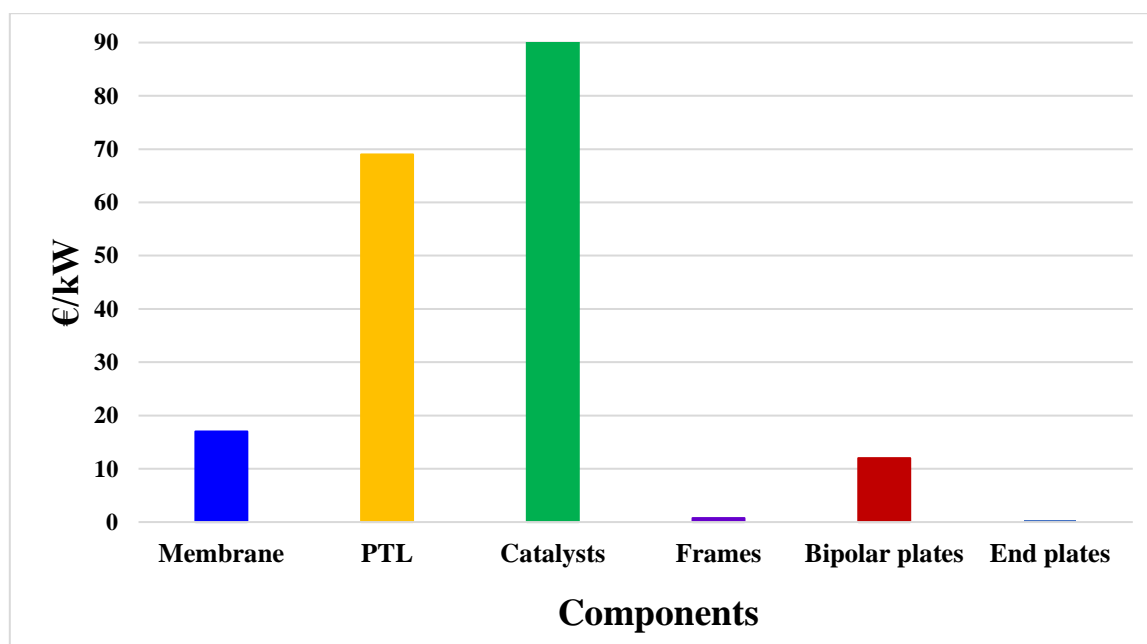The detailed PEMEL stack costs [4], show that the main cost contributors are the catalytic materials, and the PTL, specifically the anodic PTL. The high costs of the catalysts can be attributed to the expensive iridium (149 €/g) [12] correlated with an actual high loading of 2-3 mg cm^{-2}, while the main cost contributor for the PTL is the expensive Ti powder (0.25 €/g) [13] required to produce the sintered porous anode. Gold, which is essential in protecting the bipolar plates also represents a major cost contributor, with a price of 56 €/g [14] and a necessary of at least 100 nm of coating.

Moreover, according to the EU Hydrogen Policy, the installed capacity of electrolysis must be ramped up from the MW scale to the GW scale (150 GW by 2030 and 1400 GW by 2050). Consequently, the iridium demand is expected to increase 500 times only considering the next 7-8 years. However, the scarcity of iridium-based catalyst materials used in PEMWE could become a potential bottleneck in the growth of this industry.

In order to seize the overall potential, the following important opportunities to support the growth of the electrolytic hydrogen markets are considered [7]:

- Reducing costs and increasing commercialization of electrolytic hydrogen production;
- Developing economically competitive applications;
- Creating and managing bulk hydrogen storage;
- Developing domestic material supplies, including recycling and PGM-free catalysts;
- Developing electrolyzer manufacturing capacity.

Significant cost reductions are scheduled to be achieved by 2030, planning a decrease in the PGM loading by a factor of 20, while for the PTL, alternative materials like 316L stainless steel or niobium powders are considered [4]. Thinner Nafion membranes (180 – 80 μm) may also contribute to a substantial cost reduction. Moreover, to address complementary cost reductions, an increase in the efficiency/current density with a 1.75 factor is also expected. Recently, the US Department of Energy released specific technical targets for PEMWE stacks and systems [15], developed based on input from industry experts and research laboratories.

Table 3. Technical Targets for PEM Electrolyzer Stacks and Systems [15]

Stack Targets	2022 status	2026 targets	ultimate targets
Cell current (A cm^{-2})	2	3	3
Cell voltage (V)	1.9	1.8	1.6
Lifetime (h)	40000	80000	80000
Degradation (mV/1000 h)	4.8	2.3	2
Costs (€/kW)	450	100	50
PGM loading (mg cm^{-2})	3	0.5	0.125
(g/kW)	0.8	0.1	0.03
Electrical efficiency (kWh/kg H$_2$)	55	51	46
H$_2$ production costs (€/kg H$_2$)	> 3	2	1

The performance, durability, and cost targets mentioned in Table 3 must be met simultaneously on the same stack or system to achieve the levelized hydrogen cost targets.

According to the literature, there are two ways to improve the electrode performance and reduce the PGM loading:

(1) use of electrode materials characterized by higher intrinsic activity i.e., higher exchange current density;
(2) use of electrode materials characterized by larger real surface area.

Correspondingly, based on the specific objectives of the DC-PEM project, described in the proposal, a significant reduction of material usage for PTL and CL combined with a reduction of manufacturing costs is considered. Furthermore, a recycling concept for the expensive catalysts as well as for the support material and the recovery of the materials used from retired equipment is planned to be established.

The main improvements refer to:
- application of alternative and cost-efficient surface modifications on the typical Ti-based PTL, such as hydration (TiH_x) which aims to provide superior electrical conductivity and stability;
- development of alternative support materials (PTL) based on sintered metal papers, highly porous metal foils, or thin sintered fiber structures of stainless steel (316L) or nickel to replace the expensive titanium;
- application of suitable surface treatments on the newly developed PTL, such as ceramic coatings (polysiloxanes or polysilazanes) by liquefied phase deposition (LPD) to improve the corrosion resistance and stability;
- development of a novel method for catalyst immobilization based on reductive sintering between TiH_x surface and IrO_2 nanoparticles.

Task 1.2. Definition of requirements - Testing protocols for PEM electrolysis

The final goal of the project is to produce a demonstrator (TRL5 as target) that meets the actual specific requirements of a PEMWE, with costs below 1000€/kW, that can be competitive with state-of-the-art electrolyzers currently available on the market.

The cost reductions planned in the project refer mainly to the minimization of the catalyst use, but also to the reduction of the cell components manufacturing costs. A novel chemically stable, with a high surface area PTL structure proposed for the anodic side, will be obtained with the aid of a paper-based manufacturing process, creating highly porous metal foils, with pore size ranging between 1000-3000 nm (60-80% porosity) and thickness value 200-300 μm, or as alternative, thin sintered fiber structures (fiber diameter < 25 μm) made of titanium, stainless steel (316L), or nickel. The production costs for PTL are expected to be significantly reduced, while the specific surface area is estimated to be considerably increased.

Furthermore, the catalysts involved in the process will be developed in order to reduce the total PGM loading, based on typical Ir-based alloys (Ir-Rh, Ir-Ru-Pt) or IrO_x, deposited directly onto the PTL, with high distribution, by electrochemical plating or sputtering methods. The PGM

total loading will be held under 3 mg cm^{-2}, according to the state-of-the-art, while the catalyst particle sizes will be considered under 5 nm.

The current report presents a set of protocols for internal use in the DC-PEM project. The testing specifications refer to the methodology applied to assess the electrocatalytic performance, efficiency, as well as corrosion resistance, and durability of the developed catalyst materials (anode system). The proposed testing protocols should enable proper guidance for the expected results, activities, and tasks described in the project, mainly regarding WP 2, WP 4, and WP 6.

The various PEM electrolyzer properties that may require characterization are regarded to evaluate the electrochemical properties and performance of the developed anodes in different settings, considering a three-electrode cell configuration, half-cell, (both *ex-situ*) and single full-cell (*in-situ*). The testing protocols refer to [16]:

- Overall performance of the PEM electrolyzer (*I-V* curves);
- Kinetic properties (exchange current density, Tafel slopes, charge transfer coefficient);
- Ohmic properties (electrolyte conductivity, contact resistance, electrode resistance);
- Mass transport properties (pressure losses, reactant/product homogeneity);
- Catalytic structure (catalyst loading, particle size, ECSA).

In-situ testing consists of static and dynamic conditions imposed on the single cell and includes also normal and out-of-normal operating conditions, to simulate the presence of potential stressors.

Furthermore, the properties of the developed catalyst materials will be evaluated in terms of structure, morphology, surface, and bulk characteristics. These *ex-situ* investigations may refer to:

• structural properties and phase identification, unit cell dimensions, crystallite dimensions - X-ray diffraction (XRD);
• surface analysis, surface area measurements, and pore size distribution - Brunauer-Emmett-Teller method (BET), electrochemical methods;
• surface morphology and microstructure, catalyst chemical composition and elemental analysis, catalyst particle size distribution - Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), EDX mapping;
• morphology, composition, and crystallography through high resolution-images - Transmission Electron Microscopy (TEM);
• contact resistance determination (DC micro-ohmmeter, using carbon paper contact and various compression forces);
• porosity determination (mercury porosimetry, He pycnometry);
• detection/identification of elements at any concentration, detection of possible impurities (ICP, Inductively Coupled Plasma);
• corrosion investigations and catalytic activity in a three-cell and half-cell configuration – electrochemical methods.

1.1.1. Testing protocol for corrosion resistance and stability assessment of the porous transport layer/catalyst layer (the anode system)

Corrosion resistance evaluation of the PTL, as well as the PTL/CL system, will be performed using electrochemical standardized methods, applying potentiostatic and potentiodynamic measurements. All measurements will be carried out using a standard potentiostat/galvanostat. The overall testing conditions are presented in Table 4. Working electrodes, in the form of disks, having an exposed surface area of 1 cm^2, will be prepared, based on the proposed anode materials. A three-electrode cell configuration is planned to be used for the electrochemical measurements, using different electrolytes to simulate the harsh PEMEL environment, under the operating conditions. O$_2$ saturated 0.05 M H$_2$SO$_4$ solutions with/without fluoride ions additions (0.1 ppm) are planned to be used, at different working temperatures, up to 80°C. The temperature of the cell will be controlled using a thermostat. F$^-$ are added in the electrolyte to simulate the proton exchange membrane degradation upon operation, which often results in fluoride ions releases. Since one of the materials proposed as PTL is based on titanium, which is the most commonly used material for BPP and PTL in PEMEL, its passivity is susceptible to being destroyed by the presence of F$^-$, especially in aqueous solutions and high temperatures, resulting in TiF$_6^{2-}$ or TiF$_6^{3-}$ formation [17]. Moreover, at the boiling point, a corrosion rate as high as 9 mm/year^{-1} was reported for titanium in 1 wt. % H$_2$SO$_4$. In the case of 316L stainless steel used for PTL, several studies [18] concluded that the corrosion resistance of this material decreased with the increase of F$^-$ concentration in the testing solutions.

Table 4. Testing conditions for corrosion evaluation

Testing conditions	Parameters
Proposed electrolyte	0.05 M H$_2$SO$_4$
	0.05 M H$_2$SO$_4$ + 0.1 ppm F$^-$ (HF/NaF as the source for the F$^-$)
Temperature	25°C
	50°C
	80°C
Purging gas	O$_2$
Purging time	30 min before testing
	continuously during testing
Working electrode	PTL disks (made of Ti/316L/Ni-based alloys) with and without catalyst (anode system) (1 cm^2 geometric surface)
	PTL/CL disks (1 cm^2 geometric surface)
Reference electrode	SHE
Counter electrode	Platinum mesh
Techniques	OCP, EIS, LSV

The corrosion testing protocol includes the Open Circuit Potential (OCP) measurement for 1 h, followed by Electrochemical Impedance Spectroscopy (EIS) at the OCP value. The potentiodynamic polarization - linear sweep voltammetry (LSV) at low scan rates will allow to evaluate the important parameters such as corrosion potential, corrosion current density, and polarization resistance. During operation, the PTL, as well as the CL, should withstand a high

operation voltage in an oxidative environment, therefore the next sequence will subject the working electrodes to a long-term stress test, at a constant potential of 2 V. Subsequently, the corrosion parameters will be evaluated again. Each PTL/CL proposed material will be repeatedly tested, to ensure the reproducibility of the results. The corrosion testing protocol consists of the procedures presented in Table 5.

Table 5. Corrosion testing protocol

Sequence	Procedure
1	OCP measurement for 1 h
2	EIS at OCP
3	Potentiodynamic polarization measurements in the $\pm$ 250 mV vs OCP range, 0.016 mV s^{-1} scan rate
4	Current measurements at 2V for 6h
5	OCP measurement for 1 h
6	EIS measurement at OCP
7	Potentiodynamic measurements in the $\pm$ 250 mV vs OCP range, 0.016 mV s^{-1} scan rate

Additionally, immersion tests for 1000 h at 90°C, in similar testing electrolytes are planned to be performed, to evaluate both corrosion resistance and stability. The results will be correlated with the values obtained from the electrochemical testing method.

1.1.2. Testing protocol for catalytic activity and stability in a three-electrode cell configuration

A similar three-electrode assembly is used for the *ex-situ* electrochemical characterization of the catalysts and the measurements are performed using sulfuric acid as an electrolyte, with and without F$^-$ additions. Similar testing conditions as in the case of corrosion evaluation are to be applied which are presented in Table 6. All measurements will be carried out using a standard potentiostat/galvanostat.

Table 6. Testing conditions for activity and stability assessment

Testing specifications	Parameters
Electrolyte	0.05 M H_2SO_4
	0.05 M H_2SO_4 + 0.1 ppm F- (HF/NaF as the source for the F-)
Temperature	25°C
	80°C
Purging gas	O_2
Purging time	30 min before testing
	continuously during testing
Electrode	PTL disks with catalysts (anode system) (1 cm^2 geometric surface)
Reference electrode	SHE
Counter electrode	Platinum mesh
Techniques	LSV, CV, EIS

OER activity testing

LSV and Cyclic Voltammetry (CV) measurements are carried out for electrochemical evaluation of the prepared catalyst systems and their catalytic activity and stability evaluation. The kinetics of O_2 evolution by voltammetry techniques will be investigated, including the determination of Tafel slopes, exchange current densities, and equilibrium potential. The measurements are performed at 25°C and 80°C, in a three-electrode cell, in which the developed anode system is employed as a working electrode, a SHE is used as a reference electrode, and a platinum mesh as a counter electrode, respectively. O_2-saturated 0.05 M H_2SO_4 is used as an electrolyte, with or without F^- additions.

All electrodes are subjected to the full protocol listed in Table 7. In the first step, the potential is swept from 1 V to 1.6 V vs. SHE with a scanning rate of 5 mV s^{-1} for electrode activation and the OER activity pre-test. In the second step, the potential is swept between 0 V to 1.6 V vs. SHE with a scanning rate of 20 mV s^{-1}, for 10 cycles, to electrochemically oxidize the catalysts. Step 3 is designed for OER activity evaluation since the electrode had achieved a steady state after step 2. After capacitance correction and ohmic resistance correction, the plot obtained in step 3 is used to compare the OER activity among all of the catalysts, in similar testing conditions. In step 4, EIS measurements will also be performed to determine the ohmic resistance.

Table 7. Activity and stability testing protocol

Steps	Technique	Start potential [V vs. SHE]	End potential [V vs. SHE]	Sweep rate [mV s^{-1}]	No. of cycles	Purposes
1.	LSV	1	1.6	5	1	OER pre-test /activation
2.	CV	0	1.6	20	10	oxidation
3.	LSV	1	1.6	5	1	OER activity evaluation
4.	EIS	at OCP				ohmic resistance determination

Stability testing

Chronopotentiometry is used to evaluate the stability of the catalysts. The measurements are carried out in O_2-saturated 0.05 M H_2SO_4 with and without F^- additions, at 25 °C and 80°C. Before stability testing, all electrodes are subjected to the full electrochemical protocol listed in Table 7 to achieve an electrochemically oxidized electrode. Afterward, the galvanostatic mode is employed, and the current density loaded on the electrode is set up to 1 mA cm^{-2} for 15 hours, while the potential is recorded.

1.1.3. Testing protocol for operation in a half-cell configuration (durability and activity towards O_2 evolution)

Half-cell experiments are convenient and relatively fast methods of analysis and screening of catalyst materials. A specialized half-cell setup will be developed for the electrochemical

characterization of experimental anode activity for O_2 evolution and durability. This setup consists of gold-plated Cu current collectors (1 mm thickness with 3 μm gold coating), a membrane separator, and a compartment with reference (Ag/AgCl saturated) and counter electrode (Pt foil 10 cm^2). The volume of the counter electrode compartment is 16 ml, containing 0.5 M H_2SO_4 solution, while the working electrode compartment contains deionized water. The active area of the tested electrodes is 4 cm^2 and the working temperature is set to 80 °C. The endplates are made of gold-plated Ti (2 mm thickness with 30 μm gold coating). Using this arrangement, the kinetics of O_2 formation by voltammetry techniques will be investigated, including the determination of Tafel slopes, exchange current densities, and equilibrium potential. At the same time, a degradation test will be performed. These tests will consist of potential cycling and constant potential polarisation in the O_2 evolution potential region. The changes in ohmic and polarisation resistance will be observed by electrochemical impedance spectroscopy (EIS) while changes in anode composition will be determined postmortem. All measurements will be carried out using a standard potentiostat/galvanostat.

Table 8. Half-cell testing conditions

Testing conditions	Parameters
Current collectors	Cu (1 mm thickness) with 3 μm gold coating
End plates	Ti (2 mm thickness) with 30 μm gold coating
Membrane separator	Nafion/Aquivion
Working electrode	PTL/CL disks (4 cm^2 active surface)
Electrolyte WE	flow of deionized water
Temperature	80°C
Reference electrode	Ag/AgCl saturated
Counter electrode	Platinum foil (10 cm^2)
Electrolyte CE	0.5 M H_2SO_4
Techniques	OCP, EIS, LSV

Table 9. Half-cell testing protocol

Sequence	Procedure
1	Potentiostatic operation at 1 V – 1.7 V vs. Ag/AgCl, 5 mV s^{-1} scan rate, for 24 h
2	Every 1 h acquisition of EIS

1.1.4. Testing protocol for operation in a single-cell (*in-situ*) configuration

The JRC and FCH2JU have published harmonized test methods for low-temperature water electrolysis to perform polarization curves and electrochemical impedance spectroscopy for the characterization of single cells and stacks. A polarization curve generally plots either voltage U [V] or power density P_d [W cm^{-2}] vs. the current I [A] or current density i [A cm^{-2}] of the cell or the stack. The polarization curve provides information about cell/stack processes, including reaction kinetics, ohmic losses, and mass transport limitation.

In-situ single-cell testing enables the evaluation of the cell performance, considering the following:

- Polarization curve (*I-V*) for the overall electrochemical performance evaluation [19];
- EIS for separating the ohmic activation and concentration losses, reaction rates, diffusion coefficients, charge transfer resistance, and double-layer capacitance;
- CV to measure reaction kinetics and ECSA;
- Stability and durability measurements;

The electrochemical testing of the system will be performed during a single-cell operation, using MEAs in the presence of different commercial membranes. The proposed membranes are Nafion/Aquivion.

Assembled MEA will be tested in a single-cell PEMWE, at conditions relevant to industrial operation. The testing conditions are presented in Table 10. The active surface area of the cell to be tested is 4 cm^2 to avoid the effects of cell flow fields and mass transport and the temperature range is limited below 80°C (ranging from 25°C to 80°C). The single-cell experiment is carried out in the potentiostatic mode, at 2V, with a continuous flow of deionized water on the anode. The single cell will be operated for at least 300 hours. During the operation, the single cell will be periodically characterized using *I-V* curves (1.4 V – 2V) and EIS (the acquisition of polarisation curves will be made every 24 hours). Using this procedure, changes in the cell ohmic resistance, and charge and mass-transfer resistances will be observed *in operando* mode. After the end of the single-cell operation, all components, including the catalyst on the cathode, membrane, and especially, the anode will be examined in detail using the set of experimental techniques for *ex-situ* characterization, as previously described, to compare the results with freshly prepared components.

Table 10. Single-cell testing conditions

Testing conditions	Parameters
Active area	4 cm^2
Current collectors	Cu (1 mm thickness) with 3 μm gold coating
End plates	Ti (GR1 2 mm thickness) with 30 μm gold coating
Membrane	Nafion/Aquivion
Flow field type	parallel
Channel width	1 mm
Sealing	Expanded or solid PTFE
Sealing thickness	According to the PTL
Max. Temperature	120°C
Max. Pressure	5 bar

MEA activation and assembly

The activation procedure of MEA is required to properly humidify the electrolyte membrane and bring the performance to its highest and steady-state level.

The activation of the membrane will be performed using the steps presented in Table 10.

Table 11. MEA activation conditions

Step	Conditions	Values
1	Medium	Deionized water
	Duration	2 h
	Temperature	80°C
2	Medium	3 wt.% H_2O_2
	Duration	30 min
	Temperature	60°C
3	Medium	0.05 M H_2SO_4
	Duration	30 min
	Temperature	60°C
4	Medium	Deionized water
	Duration	1 h
	Temperature	80°C
Storage of membrane in deionized water at the laboratory temperature.		

Two MEA assemblies are proposed:

MEA assembly option 1 - deposition of cathode catalyst layer directly on the membrane by ultrasonic spray coating and assembly with the cathode carbon PTL and anode.

MEA assembly option 2 - hot-pressing of the activated membrane, commercial or in-house prepared cathode and anode, at temperature of 120 °C, pressure of 5 bar, for 10 min. After hot pressing, a reactivation of MEA in deionized water at 80 °C for 2 h is performed.

MEA testing

After the MEA activation, performance testing is initiated to provide significant data on cell operation in the given testing conditions. Several electrochemical measurements are planned daily, such as polarization curves, cyclic voltammetry, electrochemical impedance spectroscopy, and durability/stability tests.

Polarization curve (*I-V* curve)

The polarization curve measurement is a basic test method used to characterize low-temperature water electrolysis (WE) single cells and stacks at specified operating conditions (temperature, T, and pressure, p).

Current density measurements are performed periodically during various stages of the cell operation. These tests are performed to verify the electrolyzer performance by applying a set of pre-defined potentials (ranging from 1.4 V to 2 V, with a 5 mV s^{-1} scan rate) and measuring the current output. At each potential, the time needed in order to get the stable current values is 30-60 seconds.

Several steps are taken into consideration, as follows:

- Precondition: The cell current density is kept at 0.1 A cm^{-2} for 5 minutes to ensure the catalysts are in the proper oxidation state.
- The polarization curve measurement is performed under potentiostatic control.
- The measurement should be aborted when the cell voltage is 2.2 V or above (cut-off voltage). A higher cut-off voltage, (for example 2.4 V), may be applied where end-of-life (EoL) testing is aimed.
- At ambient pressure, it is recommended that a polarisation curve measurement from lowest to highest current density (ascending polarisation curve) be performed, followed by a polarisation curve measurement in reverse order (descending polarisation curve).

EIS measurements

EIS is a suitable and powerful diagnostic method for PEMWE [20]. The objective of EIS measurements is to determine the polarization cell resistances. EIS spectra will be recorded in the potentiostatic mode at several selected potential values (1.4, 1.6, 1.8, and 2 V). The EIS measurements parameters are presented in Table 12.

Table 12. EIS measurements parameters

Conditions	Values
Voltage	1.4; 1.6; 1.8; 2 V
Frequencies	0.1 Hz – 18 kHz
Frequencies per decade	10
Amplitude	5% of voltage
Number of frequencies	50
Frequency step	logarithmic
Wave type	Single sine

CV measurements

CV is employed to investigate *in-situ* oxidation/reduction processes by studying electron transfer chemical reactions. It is commonly used in the development of electrocatalysts as a screening tool to evaluate catalytic activity and ECSA. It allows the in-situ study of the catalyst utilization and the investigation of the ionomer-catalyst interface when different ionomers are used [21]. In CV, the potential of the PEMWE cell is linearly swept at a constant scan rate v from the start potential, E$_{initial}$ to the end potential, E$_{final}$ to be reversed to the start potential creating a symmetrical triangular potential waveform while recording the Faradaic (i.e. by redox surface reaction) and capacitive (double layer charging of the electrode-electrolyte interface) current response known as cyclic voltammogram (profile of current or current response versus potential). During the measurements, humidified hydrogen and water are fed into the hydrogen evolution and oxygen evolution reaction electrode, respectively. The recommended conditions to be followed during CV measurements are listed in the following table, including reference operating conditions during the measurements as well as potentiostat parameters set. A sweep scan rate of 20 mV s^{-1} is highly recommended, but other scan rates could also provide valuable information as well. The CV measurement parameters are presented in Table 13.

Table 13. CV measurement parameters

Conditions	Values
Cell temperature	80 °C
Cell pressure	Atmospheric/100 kPa
Water flow rate	10 cm^3 min^{-1} cm^2_{geo}
Start potential, $E_{initial}$	0.4 V
Upper vertex potential, E_{vert1}	1.4 V
Lower vertex potential, E_{vert2}	0.4 V
End potential, E_{final}	0 V
Step potential	0.008 V
Scan rate	5 – 100 mV s^{-1}
Number of scans	5 – 30 scans

Stability test

Long-term testing under constant operating conditions is also the simplest and most practical way to study PEMWE degradation. The obtained result of the degradation test is affected only by the duration of the test, the operating point, and the temperature. Depending on the duration, such tests in the literature are called either stability tests or long-term tests. State-of-the-art PEM electrolyzers have a lifetime of 20.000 h with an average degradation rate of up to 14 µV/h [22]. Steady-state response for 2000 h of operation of the cell will be evaluated at a constant current density (at 4 A cm^{-2} at rated power and 6 A cm^{-2} at overload mode). Post-mortem analysis will be performed after accelerated stress conditions at a selection of MEAs through cross-section SEM and EDS analysis, thus investigating the long-term stability of each of the system components, in combination with elemental/structural analysis and MEAs thickness and degradation issues.

Concluding remarks

All the testing and operating protocols reported in this document were decided through a series of discussions between DC-PEM partners, according to FCH2JU harmonized specified guidelines and DOE protocols.

All the procedures and techniques reported in the current document have been described to optimize the electrocatalysts, MEA, stack, and PEM water electrolysis system in terms of activity, durability, stability, and efficiency, thus providing a specific approach to achieve the project's milestones.

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