



Deliverable Report

Compliance test protocols and analytics

(D2.2)

<http://pretzel-electrolyzer.eu/>

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Project 779478 - PRETZEL

Novel modular stack design for high pressure PEM water electrolyzer technology with wide operation range and reduced cost

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Acronyms

Acronym	Meaning
AAS	Atomic Absorption Spectroscopy
BET	Brunauer-Emmett-Teller
BPP	BiPolar Plate
CV	Cyclic Voltammetry
EDX	Energy Dispersive X-Ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
GC	Glassy Carbon
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IV	Current-Voltage
MEA	Membrane Electrode Assembly
OCP	Open Circuit Potential
OER	Oxygen Evolution Reaction
OPD	Overpotential Deposition
PEMEL	Proton Exchange Membrane Electrolyser
RDE	Rotating Disc Electrode
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction

1 Introduction

Deliverable 2.2 describes the protocols for characterizing the PEM electrolysis system components as well as the test plan and protocols of the system design and the electrochemical performance. The aim of this work package is to develop characterization and evaluation protocols for the components of the PEM electrolysis system. Testing Protocols will be developed and applied through the project for the single cell and stack investigation, facilitating the assessment of the single-cell performance and of the short stack under specified conditions, while providing preliminary pre-normative results that lead to recommended practices for the concept and the development of market-oriented specifications. Development of the protocols will be based on partners' testing practices/protocols as well as available FCH JU harmonized testing procedures developed by the JRC in collaboration with European industry and researchers.

2 Protocols for PEM electrolysis system components

2.1 Properties of the electro-catalysts

In order to assess the electro-catalysts properties, a number of methods will be applied either in the form of physicochemical testing or through electrochemical applications, such as RDE measurements. Corrosion testing will also be performed and analyzed, to establish a set of characteristics in terms of durability, performance and efficiency. Thus, in this project a proper plan for PEM electrolysis test activities could be enabled for WP3 to WP6.

2.1.1 *Physico-chemical characterization*

Optimization of the electro-catalyst properties will be achieved in this project in order to have the most efficient electrochemical performances. A catalyst support is essentially used for the anode materials, developing materials of iridium and mixed oxides of iridium and ruthenium supported on ATO, while at the cathode carbon black catalyst support is necessary to achieve efficient performance of platinum. Catalyst properties are assessed in terms of structure, morphology, surface and bulk characteristics. Such properties are

- structural properties, phase identification of crystalline materials, unit cell dimensions (XRD, X-Ray Diffraction)
- surface analysis, surface area measurement, pore size distribution (BET, Brunauer-Emmett-Teller)
- surface morphology and examination through microscopy images, catalyst composition and elemental analysis (SEM, Scanning Electron Microscopy and EDX, Energy dispersive X-ray spectroscopy)
- morphology, composition, crystallography through high resolution-images (TEM, Transmission Electron Microscopy)
- detection/identification of elements at any concentration, detection of possible impurities (ICP, Inductively Coupled Plasma).

2.1.2 Electrochemical testing of catalysts – RDE Measurements

Electrochemical testing of the catalysts is performed directly on glassy carbon electrode during RDE (Rotating Disc Electrode) measurements, to recognize the effect of synthesis conditions and different materials on the OER (Oxygen Evolution Reaction) electrochemical activity. A three-electrode assembly is used for the electrochemical characterization of the catalysts and the measurements are performed by using sulfuric acid as an electrolyte. Guidelines for the ink preparation and the conditions of studying the OER activity are listed and described below.

Table 1. RDE measurement conditions

RDE conditions	Options - Selected values
electrolyte solution	0.05M H ₂ SO ₄
electrolyte temperature, °C	25
bubbling gas	N ₂
time of bubbling, before measurement, min	10
rotation speed, rpm	1600
type of electrode	GC disk (diameter 3 or 5 mm)

Catalyst Ink Preparation:

10 mg catalyst
8.3 ml ultra-pure water
0.040 ml Nafion solution
30 min sonication
drop-cast on the electrode
drying under gas atmosphere

The procedure for the RDE electrochemical testing of catalysts is described in publications by the DLR research team, e.g. Wang et al.¹

Electrode preparation

A glassy carbon rotating disc electrode (area of 19.625 mm² or 7.065 mm²) is used for all electrochemical characterization. Before any measurement, the GC-RDE is polished with an alumina suspension until a fresh GC substrate is reached, achieving a mirror-like surface. Then it is cleaned by deionized, double distilled water with repeated ultra-sonication. Catalyst ink is prepared by mixing 10 mg of catalyst powder plus 40 µL of Nafion resin solution (5 wt. %), dispersed in 8.3 mL ultra-pure water. Ultra-sonication in a bath (with water temperature maintained below 40°C) for 0.5 h is performed to obtain a homogeneous catalytic ink. Then the 10 µL ink is dropped and coated on an as-prepared 5mm diameter GC-RDE surface, drying in an Ar atmosphere at room temperature. Overall catalyst loading on each electrode regardless the area is 60 µg cm⁻².

¹ L. Wang, F. Song, G. Ozouf, D. Geiger, T. Morawietz, M. Handl, P. Gazdzicki, C. Beauger, U. Kaiser, R. Hiesgen, A.S. Gago, K.A. Friedrich, J. Mater. Chem. A. 5 (2017) 3172–3178.

OER activity evaluation

Cyclic voltammetry (CV) is carried out for electrochemical oxidation of the as-prepared catalysts and their activity evaluation. The measurements are performed at 25 °C in a three-electrode cell, in which GC-RDE is employed as a working electrode, reversible hydrogen electrode (e.g. RHE, Gaskatel) and platinum foil are used as a reference electrode and a counter electrode, respectively. N₂-saturated 0.05 M H₂SO₄ is used as an electrolyte. All catalyst coated electrodes are subject to the full protocol listed in Table 2. In Sequence 1, under a rotating speed of 1600 rpm, the potential is swept from 1 V to 1.6 V vs. RHE with a scanning rate of 5 mV s⁻¹ for electrode activation and the OER activity pre-test. Then in Sequence 2, the potential is swept between 0 V to 1.6 V vs. RHE with a scanning rate of 20 mV s⁻¹, to electrochemically oxidize the catalysts. Sequence 3 is designed for OER activity evaluation since the electrode had achieved a steady state after Sequence 2. After capacitance correction and ohmic resistance (ca. 34 Ω) correction, the first cycle of Sequence 3 is used to compare the OER activity among all of the catalysts. All the measurements will be carried out by using standard potentiostat/galvanostat. EIS measurements will also be performed in order to determine the ohmic resistance between GC-RDE and RHE.

Table 2. Electrochemical measurement protocol.

Seq. No	Start Potential / V vs. RHE	Potential range / V vs. RHE	Sweep rate / mV s ⁻¹	Number of cycles	Purposes
1	1.0	1.0 – 1.6	5	3	OER activity pre-test
2	OCP	0.0 – 1.6	20	10	Electrochemical Oxidation
3	1.0	1.0 – 1.6	5	3	OER activity evaluation

Stability measurements

Chronopotentiometry is used to evaluate the stability of the catalysts. The measurements are carried out in N₂-saturated 0.05 M H₂SO₄ under a rotating speed of 1600 rpm. A fresh electrode is prepared and initially applied with the full electrochemical protocol listed in Table 2 to achieve an electrochemically oxidized electrode as well as to make sure that the target electrode could work properly. Afterwards, the galvanostatic mode is used, and the current density loaded on the electrode is set up to 1 mA cm⁻²; in the meantime, the potential is recorded. The duration of the stability test is 15 hours, and the measurements automatically stopped when the potential on target electrode reached 2.0 V vs. RHE to protect the glassy carbon electrode.

For the purpose of further confirming catalyst stability, a “duty-cycle” protocol is applied, which is proposed by Strasser and co-workers to simulate the dynamic working conditions of a PEM electrolyzer². The protocol offers a harsher working environment than the normal chronopotentiometry measurement under a constant current density. Again, as-prepared fresh electrodes are used for this independent measurement and are pre-treated by the protocol

² H. N. Nong, H.-S. Oh, T. Reier, E. Willinger, M.-G. Willinger, V. Petkov, D. Teschner and P. Strasser, *Angew. Chemie Int. Ed.*, 2015, 54, 2975–2979.

listed in Table S1. Following, the first duty cycle is applied. In brief, the electrode potential is initially kept at $E^{0.5}$ (at which the current density is 0.5 mA cm^{-2} selected from the activity evaluation curve performed in advance) for 10 min; then, the potential is increased by a step of 20 mV ($E^{0.5}+20 \text{ mV}$) for another 10 min, and the potential step increase is repeated 5 times until the final potential ($E^{0.5}+100 \text{ mV}$) is reached. For each duty-cycle, the electrode is loaded with a varied potential for 1 h. Between every two duty-cycles, two cycles of CV are performed in the OER region to evaluate any change in activity. For each catalyst, the “duty-cycle” measurement stops when the electrode could not reach 1 mA cm^{-2} up to 2.0 V vs. RHE. The maximum applied duty cycle number is 15.

2.2 Corrosion test analysis

Corrosion resistance testing of the bipolar plates will be performed on two different samples made of thick Cu sheets with a coating of dense Nb and thin Cu sheets with a coating of less dense Nb. Electrochemical measurement are to be carried out in a three-electrode configuration cell in O_2 saturated 0.05 M H_2SO_4 solution at high temperature, 90°C , to simulate the PEMEL environment under operating conditions. Supplementary, corrosion tests will be performed in the presence of 0.1 ppm fluoride ions to simulate conditions due to the proton exchange membrane degradation by fluoride emission. An overview of the corrosion test conditions is given in table 3.

Table 3. Corrosion Test measurements

Corrosion Test Conditions	Options - Selected Values
Samples to be measured - Option 1	Nb (dense)/ Cu (thick sheets)
Samples to be measured - Option 2	Nb (less dense) / Cu (thin sheets)
Solution pH	2-3
Temperature	90°C
H_2SO_4 concentration	0.05M, O_2 saturated
HF concentration	0.1 ppm

Disc shaped samples of the BPP will be prepared by grinding with SiC paper #1200, #2400 and #4000, followed by rinsing with distilled water. Samples will be mounted in a holder, leaving exposed a surface of 1 cm^2 . Solution temperature will be controlled with a thermostat.

The corrosion testing protocol includes the measurement of open circuit potential for 1 h, followed by electrochemical impedance measurement at the corrosion potential and by a potentiodynamic scan at low scan rate. This sequence of procedures will allow to evaluate important parameters such as corrosion potential, corrosion resistance and polarization resistance. During operation the BPP should withstand a high operation voltage in oxidative environment, therefore samples will be subjected to long term test at constant potential of 2 V. Afterwards, corrosion parameters will be again evaluated. An overview of the corrosion testing protocol is given in table 4.

Table 4. Corrosion Test Protocol

Corrosion testing procedure
1. OCP determination for 1h
2. EIS measurements at OCP
3. Potentiodynamic– 1 mV s^{-1}

4. Current measurements at 2V for 6h
5. OCP determination for 1h
6. EIS measurements at OCP
7. Potentiodynamic– 1mV s ⁻¹

Similar measurement will be carried out for bulk Nb and the corrosion parameters of Nb coatings will be compared to those of bulk Nb. It is expected to reach corrosion rates of 0.01 – 0.03 mm/year.

The presence of Cu corrosion products in the solution after the corrosion testing procedures will be determined by either AAS or ICP-MS.

3 Protocols for PEM electrolysis system testing

Electrochemical testing of the system is performed during a single cell operation, employing membrane electrode assemblies (MEA) in the presence of Nafion membranes. The active surface areas to be tested are of 4, 25 or 100 cm² and the temperature range is limited below 100°C. Activation and testing procedures for the MEAs to be developed within PRETZEL project, will be performed as described in the following sections.

3.1 Membrane Electrode Assembly (MEA) activation

The activation procedure is necessary for any MEA, in order to properly humidify the electrolyte membrane and bring the performance to its highest and steady-state level. The pre-treatment procedures include all the actions carried out on a fresh MEA, in order to increase the performance and enhance the system's stability and activity. Selected values of the operating parameters during MEAs activation procedure are listed below. Water flow rate values depend on the current density at each system, since 0.336 cm³ h⁻¹ of water corresponds to exactly 1A of current, but the total amount of water supply is always in excess, to ensure proper humidification and avoid water starvation.

Table 5. MEA activation conditions

Activation conditions	Selected values
Temperature, °C	70-80
Pressure	atmospheric
Water Flow Rate (anode), cm ³ h ⁻¹	1-100
Helium Flow Rate (cathode), cm ³ min ⁻¹	100
Water Inlet Temperature, °C	70
Water Inlet Pressure	atmospheric

MEA activation procedure is completed after two days of conditioning under the pre-mentioned conditions, with repeated daily polarization curves and EIS measurements.

Table 6. MEA activation protocol

MEA activation procedure
Day 1
1. Operating Temperature @ 70°C
2. OCP determination
3. IV measurements/EIS measurements @ 1.3-2.2 V
4. Repeat for 3-4 times
Day 2
1. Operating Temperature @ 80°C
2. OCP determination
3. IV/EIS measurements @ 1.3-2.2 V
4. Repeat for 3-4 times
Day 3
MEA testing

3.2 Membrane Electrode Assembly (MEA) testing

Having the MEA conditioned, the performance testing is starting in order to provide data on cell operation at the given conditions. A number of electrochemical measurements are planned on a daily basis, such as polarization curves, cyclic voltammetry, electrochemical impedance spectroscopy and durability/stability tests.

3.2.1 Operating parameters

The operating conditions during MEAs testing are the selected ones, similarly to the activation procedure. The selected values and a typical procedure during basic activity evaluation experiments are listed below.

Table 7. MEA testing conditions

MEA testing - Operating Conditions	Selected Values
Temperature, °C	70
Pressure - option 1	atmospheric
Pressure - option 2	up to 10bar
Water Flow Rate, cm ³ h ⁻¹	1-100
Helium Flow Rate, cm ³ min ⁻¹	100
Water Inlet Temperature, °C	70
Water Inlet Pressure	atmospheric

Table 8. MEA testing protocol

MEA Testing Procedure
1. break-in
2. OCV determination for 5min

3. Applied voltage of 1.8 V for 1 h, until stable
4. IV and EIS measurements at 1.3 V-2.2 V
5. repeat the procedure up to 4 times
6. MEA overnight idle
7. Repeat the daily procedure for 8-10 days
8. Stability MEA test at 1.8 V (applied voltage) for 8hrs
9. CV measurements under H ₂ flow
10. IV and EIS measurements at 1.3 V-2.4 V

3.2.2 Measurements of current-voltage polarization curves

Typical performance data will be collected, according to the following table. Current density measurements are performed periodically during various stages of the cell operation. This test is used to verify the electrolyzer performance by applying a set of pre-defined electric potential and measuring the current output. At each potential, the time needed in order to get the stable current values is 30-60 seconds.

Table 9. Current/voltage polarization curves data

Applied Voltage (V)	Current Density measured (A cm ⁻²)
1.3	
1.4	
1.5	
1.6	
1.7	
1.8	
1.9	
2.0	
2.1	
2.2	

3.2.3 Electrochemical Impedance Spectroscopy measurements

The objective of EIS measurements is to determine series and polarization cell resistances. EIS spectra are recorded in potentiostatic mode at each of the values of the polarization curves or at a number of selected ones.

Table 10. EIS measurements parameters

Conditions of EIS measurements	Selected values
Voltage Range, V	1.3-2.2
Frequencies Range	0.1 Hz – 1 MHz
Number of frequencies per decade	10

Amplitude	0.01V _{RMS}
Number of frequencies	50
Frequency Step	Logarithmic
Wave type	Single sine
Maximum Integration Time	0.125 s
Lowest Current range	10 nA
Highest Current range	20 A

3.2.4 Cyclic Voltammetry measurements

Cyclic Voltammetry is employed to investigate oxidation/reduction processes studying electron transfer chemical reactions. The aim of these measurements is to determine the electrochemically active surface area of the electro-catalyst.

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 20mV s⁻¹ is highly recommended, but other scan rates could also provide valuable information as well.

Table 11. CV measurements parameters

CV measurements conditions	Options - Selected values
Operating Temperature, °C	70
Operating Pressure	atmospheric
Water flow rate (anode), cm ³ h ⁻¹	1-100
Helium flow rate (cathode), cm ³ min ⁻¹	100
Start potential, V	0,4
Upper vertex potential, V	1,4
Lower vertex potential, V	-0,008
Stop potential, V	0
Step potential, V	0,008
CV scan rates, mV s ⁻¹	5-100
number of CV scans	5-30
Number of stop crossings	10 (for 5 scans), 60 (for 30 scans)
Estimated number of points	1850

3.2.5 Stability test

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.

After a series of experimental measurements at the most promising materials produced and since each system component will be optimized in terms of activity and stability, a PRETZEL electrolyzer stack will be integrated in order to determine the stability during a long-term test run.

4 Concluding remarks

All the testing and operating protocols reported in this document were decided through a series of discussions between PRETZEL partners, in accordance with FCH JU harmonised specified guidelines and protocols.

All the procedures and techniques reported have been described in order to optimize all the components, MEAs, 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.