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pressurised hydrogen production

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Advanced High Pressure and Cost-Effective PEM
Water Electrolysis Technology

ADVANCEPEM – Deliverable Report

D2.1 – Harmonised test protocols



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Publishable summary

A benchmark for electrolyser components against which development progress can be assessed in terms of durability, performance and cost is established. Harmonised terminology, procedures and characterisation protocols developed in previous FCH JU/ CLEAN HYDROGEN JU projects are implemented for high pressure and high temperature PEM electrolyser systems. Ex situ and in situ characterisation of membranes, catalysts, electrodes, and MEA assessment in single cell testing is addressed. Protocols to assess stack and system durability, dynamic behaviour and degradation in steady-state and accelerated stress tests are implemented. A protocol for stack failure analysis and procedures relating to safety issues and response plan as well as to the procedures for validation of quantitative project targets is established. Testing procedures for single cells, stacks and electrolysis systems under standard operating conditions are established in accordance with the Harmonised Testing Procedures by the European Commission Joint Research Centre (JRC). The collaboration with JRC addresses a further development of test protocols and procedures for performance and durability assessment of electrolysers operating at high pressure and temperatures. The project will provide information to JRC on safety aspects for advanced high temperature, high pressure electrolyser technology. Safety-related events that may occur during the execution of this project will be reported to JRC who manage the European hydrogen safety reference database, HIAD.

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1 Summary

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2 Introduction

The testing procedures developed in ADVANCEPEM deal with characterisation protocols for stack components, such as membranes, catalysts and MEAs, stack and system devices for operation under conditions which are relevant to the achievement of project targets. The aim is to align consortium procedures with the harmonised test protocols and parameters defined by the Joint Research Laboratory of the European Commission (JRC-IET) for PEM water electrolysis.

The protocols here defined extend those addressed in the harmonised JRC test protocols. They include procedures for screening membranes, anode and cathode catalysts, as well as MEAs, prepared by various manufacturing methods, to address the operating conditions applied in ADVANCEPEM. Moreover, the aim is to allow for a comparison of the results achieved in different consortium laboratories. The defined procedures and terminology allow a quantitative assessment of the project targets with regard to performance, durability, and dynamic behaviour. A wide range of current densities, temperature and pressures is addressed extending the range of the stressors identified in the harmonised testing procedures from JRC.

The envisaged collaboration with JRC extends beyond the set of protocols and procedures used in ADVANCEPEM and includes information on the safety aspects for high pressure and high temperature operation in PEM electrolysis technology. Any safety-related event that may eventually occur within ADVANCEPEM will be reported to the European Commission's Joint Research Centre (JRC), who manage the European hydrogen safety reference database, HIAD.

The aim of these harmonised test protocols is to provide a fair comparison of the results and achievements within the different organisations and programs. Their application may be extended to other projects addressing high pressure and temperature operating conditions. A section on terminology is implemented in ADVANCEPEM to define Key Performance Indicators (KPIs). In some cases, more than one test protocol is planned to define KPIs; the same applies to the definition of the set of parameters.

The protocols relevant to the definition of KPIs are both based on ex-situ and in-situ testing procedures. Ex-situ testing relates to the components such as the membrane and catalysts. Whereas, the in situ testing regards the electrochemical assessment of the devices (cells, stack and system) e.g., in terms of polarization (voltage vs. current density or J-V) curves, beginning of test (BoT) and end of test (EoT), to determine parameters such as performance, efficiency and voltage decay (performance loss) in a wide range. Relevant tests include constant load (current) operation, and dynamic load operation with specific current profiles. These are applied to stack and system (containerised stack with balance-of-plant) to address real operating conditions in an industrially relevant environment.

Diagnostic procedures such as electrochemical impedance spectroscopy (EIS), gas cross-over and water analysis are part of the testing protocols since they play an important role in understanding degradation phenomena originating from operation. These methods can be used for in-situ diagnostics and EoT characterisation of electrochemical devices (cell, stack, system). Post operation analysis is performed after cell or stack disassembly to assess degradation mechanism(s) including in-depth analysis of active MEA components e.g., electrocatalysts, membranes and stack components assessment such as PTLs. Post-operation analysis will be carried out through advanced characterisation techniques such as XPS, XRD, SEM, TEM, EDX. This will allow study of degradation phenomena and will provide a basis for future improvements.

3 Procedures and protocols for assessing PEM water electrolysis components

3.1 Water electrolysis membrane assessment

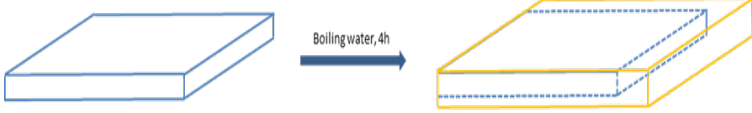
Polymer electrolyte water electrolysis membranes play an important role in electrolyser performance at high current density, in reducing the gas cross-over at high operating pressures and high temperature operation.

Unlike Nafion™ that cannot operate at temperatures above 90 °C because of the low glass transition temperature, the AQUIVION® membranes developed in ADVANCEPEM significantly extends the operating temperature range. To avoid damaging the membrane under critical conditions, the system is operated at 0.5-1 A cm⁻² current density (10-20% partial load), to avoid that the hydrogen concentration at the anode reaches the lower explosion limit (4% hydrogen in oxygen). At very low current density, the hydrogen concentration at the anode, related to the H₂ permeated by diffusion, can rise significantly in the absence of the dilution effect produced by the oxygen evolution at high rate. The high pressure is also important to address operation above 90 °C to avoid membrane dehydration with consequent decrease of proton conductivity.

Operation at high current density requires reducing the ohmic drop to limit efficiency losses. This can be achieved by significantly increasing the membrane conductivity by using thin membranes. Differential operation (pressurised hydrogen and non-pressurised oxygen) can reduce safety issues at the anode; however, gas cross-over is exacerbated by both a low thickness and low EW of AQUIVION® membranes. Moreover, high pressure operation causes mechanical stresses on the membrane. This can be addressed by improving mechanical properties e.g., using a reinforcement. Proton conductivity, cross-over, swelling, and glass transition temperature are important parameters that affect the membrane performance under ADVANCEPEM operating conditions.

3.1.1 Thermal, chemical and mechanical stability properties

Thermal and chemical stability assessment	
Membrane Conditioning	1 M H ₂ SO ₄ at T = 80 °C for 5 hours, rinse and store in demineralised water Measure the thickness of the hydrated membrane prior to cell assembly
Test Method: <i>Thermal Stability</i>	<ul style="list-style-type: none"> • Carry out thermal analysis under ThermoGravimetric Analysis (TGA-DSC) mode • Vary the temperature from ambient to 900 °C in air or nitrogen atmosphere at a heating rate of 2 °C min⁻¹. • Measure weight losses accordingly • Associate weight losses to degradation processes
Test Method: <i>Glass transition temperature</i>	<ul style="list-style-type: none"> • Carry out Dynamic Mechanical Analysis (DMA) to study viscoelastic properties of the polymer electrolyte under mechanical force relevant for operation under high differential pressure (up to 100 bar). • Vary temperature from ambient to 400 °C in air at a heating rate of 2 °C min⁻¹, sampling rate 1 Hz. • Report T_g at maximum of tan(δ) • Glass transition temperature defines the maximum operating temperature of the membrane under full hydration conditions
Test Method: <i>Chemical and Hydrolytic Stability</i>	<ul style="list-style-type: none"> • Release of fluorine species is measured as function of time during time-tests under electrolysis conditions. • Fluoride (F⁻) species are determined with an ion-selective electrode connected to a voltage and pH meter • The pH and fluoride concentrations are measured both for the anode and cathode water outlets
Test Method: <i>Oxidative Stability</i>	<ul style="list-style-type: none"> • Samples will be cut from a larger sheet of membrane once the sheet has been hydrated • Fenton's Test – Reagents: 15% H₂O₂ (200 g), Fe(NH₄)₂(SO₄)₂*6H₂O (0.05 g) and H₂SO₄ 0.5M (0.025 g) • In a plastic bottle expose 0.3 g of membrane to the above reagents 4 h at constant temperature of 75 °C and, optionally, at 90 °C (nominal operation). • The sample is removed, and the solution is cooled down till room temperature. • Measure mass loss and report as percentage of the initial mass • Measure fluoride release by lanthanum fluoride sensitive electrode
Test Method: <i>Mechanical stability</i>	<ul style="list-style-type: none"> • Apply stress-strain method ASTM D638 type V (23 °C, 50% RH) with a speed 0.25 mm min⁻¹. • If applicable repeat the same test at different temperatures relevant for the application • Determine relevant mechanical resistance parameters (Young's modulus, stress/strain at break, yield stress/strain)

<p>Test Method: <i>Dimensional swelling</i></p>	<ul style="list-style-type: none"> • Membrane immersion for 4 h in water at the relevant temperature, e.g. 80 °C, in a closed glass or plastic bottle. • Rectangular samples with equal numbers cut in machine and transverse direction • Mass measured in grams to 4d.p.; Length measured across centre of longest side in mm to 2d.p.; Thickness measured in mm to 3d.p. • Samples then dried to constant mass in desiccator % Linear Expansion Coefficient (LEC) is defined by: % LEC = ((hydrated length – initial length) / initial length) * 100 
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METRIC	FREQUENCY	TARGET
Glass transition temperature		>140 °C
Fluoride species release during steady-state operation at 4 A cm ⁻² (cathode and anode outlet)	Measured every 100 h	<0.06 ppm

3.1.2 Proton conductivity and gas permeation through the membrane

Perfluorosulfonic membranes are characterized by interrelated parameters such as exchange capacity, water uptake and proton conductivity. A decrease of equivalent weight may cause an increase of membrane conductivity and water uptake but a decrease of mechanical/chemical stability as well as an increase of gas cross-over. Assessment of these properties are thus grouped together. Hydrogen cross-over is commonly one order of magnitude higher than oxygen cross-over in proton conducting membranes, and this will be further exacerbated by the high differential pressure across the membrane in ADVANCEPEM. Thus, monitoring the hydrogen cross-over is pertinent since the system is operated under differential pressure with pressurised hydrogen and non-pressurised oxygen. The hydrogen is purified at the outlet of the stack and any traces of oxygen that may have permeated can be removed. Oxygen cross-over has been treated in previous projects dealing with balanced pressure. Here, the hydrogen cross-over protocol is updated for the targeted applications. Area specific resistance (series resistance) for the membrane is determined taking the membrane thickness and the intrinsic ionic conductivity into consideration. This parameter directly influences ohmic drop at high current density.

Exchange capacity, Water uptake, Proton conductivity, Area specific resistance, Gas cross-over Protocol and Metrics

Membrane Conditioning	1 M H ₂ SO ₄ at T = 80 °C for 5 hours, rinse in demineralised water and store in demineralised water Measure the thickness of the hydrated membrane prior to cell assembly
Test Method:	<ul style="list-style-type: none"> • Dry membrane (vacuum treatment 2 h at 105 °C) is weighted.

<p><i>Membrane exchange capacity</i></p>	<ul style="list-style-type: none"> • Equilibration of > 1 g membrane in known excess ($[\text{NaOH}]_{\text{ex}}$) of 0.1 NaOH at room temperature for 4 hrs • Titration of $[\text{NaOH}]_{\text{ex}}$ with 0.1 M HCl ($[\text{NaOH}]_{\text{tit}}$) • IEC in meq g^{-1} (3 d.p.) measured by titration as difference $[\text{NaOH}]_{\text{ex}} - [\text{NaOH}]_{\text{tit}}$ • Equivalent weight (EW) determined according to: 1 eq = 1 mol of SO_3H • EW measured in g eq^{-1}.
<p>Test Method: <i>Membrane water Uptake</i></p>	<ul style="list-style-type: none"> • Soaking pre-weighed (W_{dry}) dried membranes (vacuum oven, 2 h at 105 °C) in boiling water. • After 4 h, equilibrated samples are rinsed in cold water (10 min) • The water deposited onto the surface is wiped off with a tissue paper and then membrane is weighted (W_{wet}). • Water uptake is calculated accordingly to equation: $\text{Water Uptake (\%)} = \left(\frac{W_{\text{wet}}}{W_{\text{dry}}} - 1 \right) * 100$
<p>Test Method: <i>Membrane Ionic Conductivity / area specific resistance</i></p>	<ul style="list-style-type: none"> • Measure membrane proton conductivity by Bekktech cell with double-distilled water or milliQ water for in-plane conductivity. • Use through plane / 4-electrode set-up by varying temperature (constant relative humidity) or relative humidity (constant temperature) • AC impedance measurement from 1 MHz to 0.1 Hz • Determine series resistance from high frequency intercept. • Assess conductivity in temperatures from ambient to 140 °C, in steps of 20 °C with pressure varying from ambient to 5 bar_{abs} with further steps of 10 bar (1, 5, 10, 20, 30, etc.). Select appropriate pressure to maintain water in a liquid state. At 140 °C the minimum pressure should be 5 bar_{abs}. • From proton conductivity and membrane thickness the area specific resistance is determined: $R*S=\rho*I$ where R is the high frequency resistance, S the surface area, ρ is the reciprocal of conductivity ($1/\sigma$) and I is the thickness.
<p>Test Method: <i>Ionomer dispersion</i></p>	<ul style="list-style-type: none"> • Mean size and distribution of particles in ionomer dispersion in solvents of different dielectric constant is determined by dynamic light scattering (DLS) • Mean size is reported in nm. Solvent type and relative dielectric constant are reported.
<p>Test Method: <i>Hydrogen cross-over</i></p>	<ul style="list-style-type: none"> • The hydrogen cross-over is measured in-situ, at MEA level, under operating conditions of temperature and pressure as targeted in the project • This is carried out by placing a H₂ sensor in-line in the oxygen gas flow or by carrying a gas chromatographic analysis of the anode gas stream e.g., using a microGC • MEA in standard electrolysis cell as discussed below with water and current flowing

	<ul style="list-style-type: none"> • Calibrated H₂ sensor (i.e., HY-OPTIMA) in-line on O₂ side, or microGC • From balanced pressure to 10 MPa (cathode pressure) delta P, 1 MPa increment • Current Density is varied in steps of 0.5 A cm⁻² from 4 A cm⁻², to 0.5 A cm⁻² and finally to 0.2 A cm⁻² (cathode pressure reduced to 5 bar_{abs} (when at >90 °C) or ambient pressure (when <90 °C), when the system is under OCV)
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METRIC	FREQUENCY	TARGET
Proton conductivity area specific resistance		>0.2 S cm ⁻¹ < 25 mOhm cm ²
% H ₂ in O ₂	Steady-state measurement at different current densities;	<2 % H ₂ in the O ₂ at partial load (e.g., 5%); <0.5 % H ₂ in the O ₂ at nominal load; Quote thickness, temperature, current density, pressure alongside values

3.2 Assessment of Electro-catalysts for PEM water electrolysis

PEM water electrolysis electrocatalysts are typically based on Ir oxides at the anode and Pt on carbon at the cathode. One of the objectives in the field of PEM electrolysis is to reduce the noble metal loading while increasing performance and stability. This means achieving low overpotentials at high current densities e.g., 5 A cm⁻² as targeted in ADVANCEPEM while achieving enhanced stability under both steady-state and cycled operation. Catalyst characterization protocols deal with the identification of physico-chemical properties such as mean crystallite size, particle size, surface area that influence the catalytic activity, assessment of overpotentials at 5 A cm⁻², assessment of catalyst durability in MEAs with the selected ionomers and the capability of managing hydrogen cross-over reduction by recombination catalysts.

3.2.1 Electrocatalysts physico-chemical properties

Physico-chemical properties of electrocatalysts

Anode and cathode catalyst powders Catalysts are usually produced as powders to form an ink with the ionomer for catalytic layer integration in MEAs

Test Method: <i>Structure, alloying, crystallite size</i>	<ul style="list-style-type: none"> • Record X-ray diffraction (XRD) to determine crystallographic structure • Determine degree of alloying from peak shift using Vegard's law (thus, crystallographic unit cell parameters vary linearly with composition for a continuous substitutional solid solution in which atoms or ions that substitute for each other are randomly distributed) • Determine mean crystallite size from peak broadening using the Debye-Scherrer method
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	<ul style="list-style-type: none"> • Report mean crystallite size in nm
Test Method: <i>Chemical properties</i>	<ul style="list-style-type: none"> • Determine the Pt content of Pt/C catalyst from thermogravimetric analysis by burning the organic fraction at 950 °C in air • Determine the content of light elements from CHSNO elemental analysis • Determine the chemical composition from X-ray fluorescence, ICP or EDX analysis and report the level of accuracy
Test Method: <i>Surface properties, core-shell structures</i>	<ul style="list-style-type: none"> • Determine the oxidation state and the atomic concentrations of the elements on the surface from X-ray photoelectron spectroscopy -XPS • Repeat XPS measurements after successive 5 kV Ar⁺ ions sputtering to determine bulk composition • Carry out chemical profile analysis of catalyst particles using combination of EDS and HAADF-STEM

METRIC	FREQUENCY	TARGET
Mean crystallite size/particle size cathode (Pt)	BoT and EoT	< 2-3 nm
Mean crystallite size/particle size anode (IrRuOx)		<5-7 nm
Electrochemical active surface area cathode (Pt)		>80 m ² g ⁻¹
Surface area anode		>150 m ² g ⁻¹

3.2.2 Electrocatalytic behavior

Electrochemical assessment of anode and cathode catalyst in a single cell is the preferred procedure to avoid interference and effects from the liquid electrolyte that may cause leaching, adsorption of anions etc.

In particular, in-situ catalyst assessment provides information about the effective catalytic activity and the catalyst-ionomer interface. However a reference electrode is necessary to deconvolute anode from cathode polarization. Moreover, series resistance determination can allow to subtract ohmic losses thus determining the pure electrocatalytic behavior. Reference electrodes very useful in this context are the dynamic reference electrode (DHE) and the reversible hydrogen electrode (RHE). The DHE can be assimilated to the RHE if the current flowing through it is very small. Both allow to get the polarization behavior of the anode and cathode operating at proper current density vs. a non-polarized (RHE) or slightly polarised (DHE) small Pt electrode facing the membrane at the cathode. In the case of the DHE a small counter electrode is needed at the anode as well. Alternatively, the hydrogen pumping mode operation is adopted to determine the cathode overpotentials at different current densities which are subtracted from the cell overall polarization to get the anode curve.

Catalysts electrochemical properties

In situ anode and cathode catalysts assessment

Catalysts are mixed with the selected ionomer in optimised amounts to form a catalytic ink. The catalytic inks are used for MEA fabrication according to the catalyst coated membrane method or the electrode coated method followed by hot-pressing (lamination).

<p>Test Method: <i>Anode polarisation using the driven mode operation</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode • Feed anode with water at the anode at rate of $4 \text{ ml min}^{-1} \text{ cm}^{-2}$ • Set temperature and pressure as required (high hydrogen pressures should be avoided for current densities smaller than 0.5 A cm^{-2}; high oxygen pressure should be avoided during high temperature operation (differential pressure is the preferred approach) • Carry cell polarization in the driven mode using the cathode as reference (RHE) and counter electrode • Polarisation data-set is acquired in the same way as for the MEA polarization. This is discussed in detail in the MEA chapter. • Determine series resistance ($R_s \equiv \text{Ohm cm}^2$) from the high frequency intercept on the x-axis of the Nyquist plot • Subtract ohmic drop from the measured polarisation curve • Report anode overpotential at 5 A cm^{-2} vs. RHE, report T and P, report noble metal loading
<p>Test Method: <i>Cathode polarisation using the hydrogen pumping mode</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at both electrodes • Feed one electrode with hydrogen at a stoichiometry at least three times larger than that required at 5 A cm^{-2}. Feed water at a rate of $4 \text{ ml min}^{-1} \text{ cm}^{-2}$ • Set temperature and pressure as required (high hydrogen pressures should be avoided for current densities smaller than 0.5 A cm^{-2}; high oxygen pressure should be avoided during high temperature operation (differential pressure is the preferred approach) • Carry cell polarization in the hydrogen pumping mode • Polarisation data-set is acquired in the same way as for the MEA polarization. This is discussed in detail in the MEA chapter. For screening purposes a potentiodynamic scanning can be used with a low sweep rate (10 mV s^{-1}) • Determine series resistance ($R_s \equiv \text{Ohm cm}^2$) from the high frequency intercept on the Nyquist plot • Subtract ohmic drop from the overall measured polarisation curve to get the overpotential curve • Split in two the absolute overpotential curve assuming similar overpotentials for both hydrogen evolution and hydrogen oxidation

	<ul style="list-style-type: none"> • Report anode overpotential at 5 A cm⁻² vs. RHE, report T and P, report noble metal loading
<p>Test Method: <i>Anode and cathode polarisation using the dynamic hydrogen electrode mode</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode • Same configuration for the small electrodes (isolated from the main electrodes) forming the DHE. • Feed anode with water at a rate of 4 ml min⁻¹ cm⁻², allow for full hydration of membrane, electrodes and DHE. • Polarise cathodically (negative vs. RHE) the Pt/C electrode of the DHE with a few mA cm⁻² (using a small battery and a variable resistor or a power supply) to allow for a small hydrogen evolution while avoiding excessive reference electrode polarisation. Use the negative electrode of the DHE (H⁺/H₂) as reference electrode (~RHE) • Set temperature and pressure as required (high hydrogen pressures should be avoided for current densities smaller than 0.5 A cm⁻²; high oxygen pressures should be avoided during high temperature operation; differential pressure is the preferred approach) • Carry out anode and cathode polarizations in the DHE mode (Fig. 1A-B) using the negative electrode of the DHE as reference (RHE) to determine separate anode and cathode polarization. The sum of anode and cathode absolute polarizations should be equal to the overall cell polarization that can be measured in parallel i.e., current is passed through the cell while anode vs. DHE, cathode vs. DHE and anode vs. cathode (cell) potentials are measured. • Polarisation data-set is acquired in the same way as for the MEA polarization. This is discussed in detail in the MEA chapter. • Determine series resistance ($R_s \equiv \text{Ohm cm}^2$) from the high frequency intercept on the Nyquist plot • Subtract ohmic drop from the measured polarisation curves • Report anode and cathode overpotentials at 4 A cm⁻² vs. RHE, report T and P, report noble metal loading

METRIC	FREQUENCY	TARGET
Oxygen evolution overpotential	Measure electrode polarisation before and after a durability or a stress test	< 200 mV IR-free vs. thermoneutral potential at 4 A·cm ⁻² with noble metal loading < 0.35 mg·cm ⁻²
Hydrogen evolution overpotential	Measure electrode polarisation before and after a durability or a stress test	<50 mV IR-free vs. RHE with Pt loading < 0.05 mg·cm ⁻²

3.2.3 Electrochemically active electro-catalyst surface area

The electrochemically active catalyst surface area (ECSA) is preferably determined in situ from CV measurements. The (ECSA) is expressed in $\text{m}^2 \text{g}^{-1}$ or in mC cm^{-2} along with the used sweep rate. The total available surface area of the catalyst ($\text{m}^2 \text{g}^{-1}$) is determined by physico-chemical methods. The catalyst utilisation, U_M , a dimensionless number reflecting the extension of the catalyst-electrolyte interface expressed as a percentage (%), is the ratio between the ECSA and the total available surface area of the catalyst.

$$U_M = \text{ECSA} / \text{Total specific surface area} \equiv \%$$

The total available surface area of an unsupported catalyst is usually determined by Brunauer–Emmett–Teller (BET) measurement using nitrogen adsorption/desorption at $-196 \text{ }^\circ\text{C}$ (liquid nitrogen boiling point).

For a supported catalyst such as Pt/C or Pd/C, the total available surface area is determined from the mean particle size assuming a spherical shape for the nanosized particles, and the mass density of the metal [Aricò et al, *Electrochimica Acta* 47 (2002) 3723/3732].

The metal surface area (MSA) is calculated according to:

$$\text{MSA} = 6 \times 10^4 / (\rho \cdot d) \equiv \text{m}^2 \text{g}^{-1}$$

ρ (g cm^{-3}) is the density and d (Å) is the average particle size.

The mean particle size is derived from transmission electron microscopy or from the broadening of the X-ray diffraction peaks (Debye-Scherrer method).

Determination of the in situ ECSA for the oxygen evolution reaction (OER) electrode is usually carried out in the driven mode. Humidified hydrogen is fed to the Pt/C HER electrode and deaerated water is fed to the OER electrode.

A flow rate of $10 \text{ ml min}^{-1} \text{ cm}^{-2}$ and a dew-point temperature equal to cell temperature can be used. In the driven mode, the cathode is used as both reference and counter electrode whereas the anode is the working and sense electrode.

Since the hydrogen evolution/oxidation is a fast process, being that the current involved in the CV experiment is relatively low, the counter-reference electrode is not significantly polarized and it can be referred as RHE.

If the ohmic resistance of the cell is sufficiently low, there is no need for IR-drop correction because the current involved is relatively low.

Recommended conditions are a sweep rate of $20 \text{ mV} \cdot \text{s}^{-1}$, between 0.4 and 1.4 V RHE, triangular sweep, reference operating temperature and ambient pressure. Using potentials lower than 0.4 V vs. RHE may produce a significant reduction of the IrO_2 (respectively IrRu oxide) and thus a change of the oxidation state and related adsorption - desorption processes.

Generally, the voltammetric charge (sum of anodic and cathodic charge densities) is related to the electrochemical active area or the density of active sites. The coulombic charge varies with the sweep rate; thus, the used scan rate must be reported along with the voltammetric charge value. A linear variation of the coulombic charge with the square root of the sweep rate can allow one to speculate about inner and outer surface of the electrode.

For the anode, the active area is obtained from integration of CV profile over the entire potential window.

Since the stoichiometry of the adsorption/desorption processes is not known for the IrO₂ (respectively IrRu oxide) anode, the ECSA cannot be determined precisely. However, the voltammetric surface charge is generally considered an indication of the electrochemical active surface area even in the case a conversion of the charge into surface area is difficult because the nature of the surface reactions is not known precisely. In this case, the determined charge may be compared to another measurement carried out under the same conditions.

In situ determination of the ECSA for the Pt/C cathode in PEMWE requires that this electrode (WE) is fed with humidified nitrogen (or inert gas) and alternatively, nitrogen saturated water is present at this electrode while the electrode with IrRu oxide (CE) is fed with de-aerated water. A Dynamic Hydrogen Electrode (DHE) is used as reference electrode.

The Pt/C working is preferably polarized in the range 0.02-0.4 V vs. DHE. This is to avoid polarising significantly the counter electrode as well as hydrogen evolution. The lower potential limit can be adjusted (e.g., 0.05 V vs DHE) to avoid hydrogen evolution; the higher potential limit allows the determination of the double layer current baseline that is subtracted from the integration of the hydrogen adsorption (Pt-H) peaks. Recommended conditions are a sweep rate of 20 mV·s⁻¹, a gas flow rate of 10 ml min⁻¹ cm⁻², a water flow rate of 1 ml min⁻¹ cm⁻², reference operating temperature and ambient pressure.

For determining the ECSA the cathodic sweep profile (adsorption) is integrated after correction for double layer charging, i.e. after subtraction of double layer charging at 0.4 V RHE. For a cathode with a Pt catalyst, a value of 210 μC cm⁻² is taken assuming one monolayer coverage for hydrogen.

Electrochemically active surface area

In situ anode and cathode catalysts assessment Catalysts are mixed with the selected ionomer in optimised amounts to form a catalytic ink. The catalytic inks are used for MEA fabrication according to the catalyst coated membrane method or the electrode coated method followed by hot-pressing (lamination).

<p>Test Method: <i>Anode electrochemically active surface area using the driven mode operation</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode • Feed anode with water at a rate of 4 ml min⁻¹ cm⁻²; feed cathode with 10 ml H₂ min⁻¹ cm⁻² • Room temperature and ambient pressure are used in this experiment • Carry CV at 20 mV s⁻¹ between 0.4 V and 1.4 V RHE in the driven mode using the cathode as reference (RHE) and counter electrode • Determine series resistance ($R_s \equiv \text{Ohm cm}^2$) from the high frequency intercept on the Nyquist plot • If needed subtract ohmic drop from the measured CV • Integrate overall charge and report in mC cm⁻² along with the selected sweep rate. Report noble metal loading.
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<p>Test Method: <i>Cathode electrochemically active surface area using the DHE mode operation</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode • Same configuration for the small electrodes (isolated from the main electrodes) forming the DHE. • Feed anode with water at a rate of 4 ml min⁻¹ cm⁻² allow for full hydration of membrane, electrodes and DHE. Feed cathode with humidified nitrogen. • Room temperature and ambient pressure are used in this experiment • Carry CV at 20 mV s⁻¹ between 0.02 V and 0.4 V RHE in the DHE mode using the DHE cathode as reference (RHE) and the anode as counter electrode • Determine series resistance ($R_s \equiv \text{Ohm cm}^2$) from the high frequency intercept on the Nyquist plot • If needed subtract ohmic drop from the measured CV • Integrate adsorption charge (cathodic branch), using the value of 210 $\mu\text{C cm}^{-2}$ for one monolayer coverage for hydrogen on Pt and the measured charge determine $\text{cm}^2_{\text{real}}$ • Roughness factor: $\text{cm}^2_{\text{real}} / \text{cm}^2_{\text{geo}}$ • Using $\text{cm}^2_{\text{real}}$ and noble metal loading determine the surface area in $\text{m}^2 \text{g}^{-1}$.
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METRIC	FREQUENCY	TARGET
In-situ anode electrochemically active surface area using the driven mode operation	Measure CV before and after a durability or a stress test	> 100 mC cm ⁻² at 20 mV s ⁻¹ sweep rate in the range 0.4-1.4 V RHE
In-situ cathode electrochemically active surface area using the DHE mode operation	Measure CV before and after a durability or a stress test	>50 m ² g ⁻¹

3.2.4 Electrocatalysts stability

Durability is as important as performance. Degradation rate is exacerbated by catalyst operation at high current density in the presence of low PGM loadings. Catalyst operation at high turnover frequency was observed to cause a progressive change of Lewis acidity characteristics with time for both Ir and Ru catalysts thus influencing their ability to promote water oxidation [Siracusano et al Nano Energy 40 (2017) 618–632]. Determination of catalyst degradation can be carried out in situ during MEA studies by determining the change in overpotentials and surface area after a durability or accelerated stress-test experiment. Electrode polarisation and surface area measurements according to the methods above reported can permit quantitative estimation of catalyst degradation. These studies are complemented by ex-situ post operation analyses.

Assessment of electrocatalyst degradation

Anode and cathode catalysts durability assessment

Catalysts are mixed with the selected ionomer in optimised amounts to form a catalytic ink. The catalytic inks are used for MEA fabrication according to the catalyst coated membrane method or the electrode coated method followed by hot-pressing (lamination).

<p>Test Method: <i>In situ assessment of electrocatalyst degradation</i></p>	<ul style="list-style-type: none"> • Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode • Feed anode with water at a rate of 4 ml min⁻¹ cm⁻² for nominal operation (5 A cm⁻² and 90 °C). This is selected to keep the temperature gradient between inlet and outlet within 2 °C (stoichiometry 500 times) up to 90 °C. The flow rate can be increased to 20 ml min⁻¹ cm⁻² at 140 °C or 8 A cm⁻². Set temperature and pressure as required, differential pressure is the preferred approach (during measurement %H₂ in O₂ must remain <3% at all current densities; at >90 °C, oxygen pressure should be no higher than 5 bar_{abs}). • Carry out MEA polarization control (see MEA chapter) • Carry out a MEA durability test of 2000 h at 5 A cm⁻² preceded by 100 h at 1 A cm⁻² for conditioning • Determined series resistance (Rs ≡ Ohm cm²) from the high frequency intercept on the Nyquist plot before and after the durability test • Carry out CV analysis and electrode polarisation analysis before and after the durability test • Determined surface area and overpotentials at 5 A cm⁻² before and after the durability test. Report noble metal loading.
<p>Test Method: <i>Ex situ assessment of electrocatalyst degradation</i></p>	<ul style="list-style-type: none"> • Determine mean particle size, particle size distribution, crystallite size, BET, structure, morphology, chemistry and surface properties of the catalysts in the electrodes (or in powder form) in a parallel experiment before the durability test. Characterisation techniques involved in this analysis are XRD, XRF, EDX, ICP, TEM, SEM, BET, XPS. • Repeat analysis of physicochemical properties where applicable after the durability test of 2000 h at 4 A cm⁻² by sampling portions of the catalytic layers. • Select relevant electrode portions of the electrodes e.g., water inlet, water outlet, gas outlet, middle region etc. • Determine variation of mean particle size, particle size distribution binding energies, oxidation states, compositional changes in the surface and in the bulk of the catalyst.

METRIC	FREQUENCY	TARGET
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In-situ variation of the anode and cathode electrochemically active surface area during a durability test	Measure CV before and after a durability test 2000 h at 4 A cm ⁻²	<5% decrease in electrochemical surface area
In-situ variation anode and cathode overpotentials during a durability test	Measure overpotentials at 5 A cm ⁻² before and after a durability test of 2000 h at 5 A cm ⁻²	<5% increase in overpotential
Ex-situ: variation of anode composition	Determine the Ir/Ru ratio before and after a durability test of 2000 h at 5 A cm ⁻²	

2.2.5 Recombination catalyst

The use of a recombination catalyst at the anode is widely recognized as a requirement to reduce the concentration of hydrogen in oxygen for safety. This can contribute to cross-over management under high differential pressure.

Assessment of recombination catalyst effectiveness

In situ recombination catalysts assessment	Recombination catalysts is integrated in the MEA during preparation
Test Method: <i>In situ assessment of recombination catalysts</i>	<ul style="list-style-type: none"> Cell equipped with Pt/C at the cathode and Ir-based catalyst at the anode Feed anode with water at a rate of 4 ml min⁻¹ cm⁻² Set temperature as required Cathode pressure is varied in steps starting from the lowest pressure to the highest pressure and reverse. Maximum pressure 20 MPa. Anode pressure is set to ambient (at <90 °C) or 5 bar_{abs} (at >90 °C) and maintained Carry out MEA polarization control (see MEA chapter) Carry out steady-state operation test of at least 30 min at 5 A cm⁻², 4 A cm⁻², 3 A cm⁻², 2 A cm⁻², 1 A cm⁻², During these tests measure H₂ concentration in oxygen according to the methods discussed above. The microGC method is preferred vs. the hydrogen sensor because of better accuracy. Determine H₂ concentration in oxygen at different differential pressures as function of the operating current density Compare cross-over results with those recorded for a MEA without recombination catalyst.

METRIC	FREQUENCY	TARGET
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Hydrogen cross-over	Measure at different pressure for MEA equipped with recombination catalyst and bare MEAs	<2% H ₂ in the O ₂ at all loads; <0.2% H ₂ in the O ₂ , after the recombination catalyst, at the nominal current density Quote temperature, pressure and current density, alongside values
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3.3 Membrane-electrode assembly assessment in single cell

The performance and durability of the membrane-electrode assemblies are assessed in single cells under the conditions targeted in ADVANCEPEM. Relevant aspects regard the determination of catalysts mass loading, performance, efficiency, durability and operation under dynamic operation.

The document “EU Harmonised Polarisation Curve Test Method for Low Temperature Water Electrolysis” released by JRC provides a set of harmonised procedures for testing electrolysis cells. ADVANCEPEM operating conditions and related protocols extend the ranges reported in harmonised JRC protocols in terms of current density up to 5 A cm⁻², pressure 20 MPa and temperature 140 °C.

3.3.1 Determination of the catalyst loading for MEAs

Catalyst loading is determined by weighing the membrane before and after deposition of the catalytic layers (preceded by a step of drying in vacuum at 80 °C for 1h). This procedure can be used especially for large area MEAs. The relative amount of catalyst and ionomer in the catalytic layer (specifically in the catalytic ink) is pre-determined by weighing. Analysis (e.g., X-ray fluorescence) can be eventually applied to the complete MEA. Alternatively, a burning procedure of a fraction of a complete MEAs from the same series (or a piece of the final MEA in the case of a large area) in a special ceramic crucible (not attacked by fluorine) at 950 °C can be carried out to determine the weight of the inorganic ashes. The relative amount of Ir, Pt and Ru in the ashes can be determined by EDX or XRF. X-ray fluorescence of the MEA is the most recommended method.

3.3.2 Cell performance

The MEA is mounted in a single cell whose design is harmonized among the project partners. Screening is first carried out in a small single cell (5, 8 or 100 cm² geometrical area) and thereafter the optimised MEAs are tested in large area cells (>400 cm²).

Reference temperature for MEA assessing is 90 °C, the *temperature range* vary from 30 °C to 140 °C in 10 °C increments.

Reference water feed rate at the anode is set to 4 g cm⁻² min⁻¹.

Differential pressure is the preferred operation. Reference cathode pressures are: 1 bar_{abs} for low pressure studies, 20-30 bar_{abs} or 200 bar_{abs} for high pressure experiments. For operation above 90 °C, the anode is pressurised at 5 bar_{abs}.

Water quality: $\rho > 5$ MOhm cm.

MEA conditioning: MEA is installed in a single cell and equilibrated at 90 °C with deionised water ($\rho > 5$ MOhm cm) fed to both compartments at ambient pressure, pre-heated to this same temperature at a flow rate of 1 g cm⁻² min⁻¹.

Conditioning is continued with an applied load of 0.2 A cm⁻² for 24 hours to favor membrane hydration, in-situ purification, and stabilisation of the anode catalyst oxidation state. This conditioning procedure is used for fast screening of MEAs. In the case of durability or cycling test, a prolonged conditioning procedure is preferably used i.e. 100 hours at 1 A cm⁻².

Electrochemical impedance spectroscopy (EIS) measurements are carried out to determine the series and polarization cell resistance. EIS spectra can be recorded in potentiostatic mode at 1.5 V, 1.8 V or at 5 A cm⁻² in galvanostatic mode (constant current density). In the potentiostatic mode, the procedure consists of applying a sinusoidal AC perturbation signal with an amplitude (peak-to-peak) of maximum 10 mV and a perturbation frequency in the 10 kHz to 10 mHz range as well as in the reverse order with 7 data points per decade in logarithmic spacing. In the case of galvanostatic mode, 10% sinusoidal oscillations is used. The impedance measurements are plotted as Nyquist plots (negative imaginary part vs. real part) and Bode plots (impedance amplitude, real and imaginary part vs. perturbation frequency and/or phase shift). The cell ohmic resistance is determined from the series resistance (high frequency intercept). The polarisation resistance is the difference between the low and the high frequency intercepts on the x-axis of the Nyquist plot.

Polarization curves (I-V) are carried out in the *galvanostatic mode* by recording the cell voltage vs. the imposed current density. The current density values are selected according to a logarithm variation.

For operation at high pressure, the performance is measured from the highest to the lowest current density (descending part of the polarisation curve); operating pressure is stabilized at the maximum current density before carrying out the polarization curve in descending mode. The H₂ concentration in the O₂ stream is monitored by a hydrogen gas sensor at each current density to avoid reaching the lower explosive limit (4% H₂ in O₂).

At low current densities, especially under high differential pressure, the H₂ concentration in the oxygen stream can increase and approach the lower explosive limit. In response, the cathode pressure is usually lowered when the H₂ concentration in the oxygen reaches 3% (ambient pressure operation is recommended to record polarisation curves in this low current density region. The *cut-off-voltage of 2.2 V* is selected. *Data collection* is carried out in steps as reported below; the dwell-time at each step is 1 min (pseudo steady state-condition). The average potential is reported at each current density. The change in the cell voltage per min, generated by variation of current is registered in a table and plotted.

Current Density [A·cm ⁻²]	Cell Voltage [V]
0.0005	
0.001	
0.002	
0.005	
0.01	
0.02	
0.03	
0.04	
0.06	
0.08	
0.1	
0.15	
0.2	
0.25	
0.35	

Current Density [A·cm ⁻²]	Cell Voltage [V]
2.2	
2.4	
2.6	
2.8	
3.0	
3.5	
4.0	
4.5	
5.0	

0.4	
0.45	
0.5	
0.6	
0.7	
0.8	
0.9	
1	
1.1	
1.2	
1.3	
1.4	
1.5	
1.6	
1.7	
1.8	
1.9	
2	

Assessment of MEA performance

Single cell polarisation curve

MEA assembling according to the project fabrication procedures.
Installation of the MEAs in single cell with related checks

<p>Test Method: <i>Single cell performance assessment</i></p>	<ul style="list-style-type: none"> • Feed anode with water at a rate of $4 \text{ g min}^{-1} \text{ cm}^{-2}$ ($\rho > 5 \text{ MOhm cm}$) • Set thermostat to the desired temperature • Cell conditioning: apply a load of 0.2 A cm^{-2} for 24 hours to favor membrane hydration, in-situ purification, and stabilisation of the anode catalyst oxidation state. • Set cut-off voltage to 2.2 V • Stabilize the selected cathode pressure (differential pressure) and temperature at the maximum current density. Use a thermostat to maintain isothermal operation at maximum current density. • Carry out the polarisation curve as defined above in descending mode after stabilising outlet water temperature at the maximum current density • Monitor H_2 concentration in oxygen at each current density • Decrease pressure at low current densities if needed (H_2 in $\text{O}_2 > 3\%$) • Repeat polarisation curve in ascending mode to check for hysteresis. • Carry out AC-impedance spectroscopy
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	<ul style="list-style-type: none"> Repeat tests at various temperatures (30-140 °C) and pressures (ambient to 20 MPa); for operation above 90 °C minimum pressure at both anode and cathode is 5 bar_{abs}. Report data as Potential (V) vs. Current density (A cm⁻²) along with temperature, pressure and catalysts loadings. Report AC-impedance spectra. The reported cell temperature is the water temperature at the anode outlet.
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METRIC	FREQUENCY	TARGET
MEA performance	BoT	>5 A cm ⁻² at 1.85 V cell ⁻¹ at T>90 °C with PGM loading <0.5 mg cm ⁻²
Gas cross-over	BoT-EoT	<2 vol % H ₂ in the O ₂ at all loads; Quote temperature, pressure and current density, alongside values

1.2.1 Determination of cell durability

An enhanced stability of the MEA will contribute to reducing the cell degradation rate at high current density (5 A cm⁻²).

Both steady state and dynamic operation affect MEA stability.

Steady state operation:

Assessment of MEA stability

Single cell durability study MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks

Test Method: <i>Single cell assessment</i>	<ul style="list-style-type: none"> Safety conditions as reported for the polarisation curve. Feed anode with water at a rate of 4 ml min⁻¹ cm⁻² ($\rho > 5$ MOhm cm) Set thermostat to desired temperature Cell conditioning: apply a load of 1 A cm⁻² for 100 hours at ambient pressure Set cut-off voltage to 2.2 V Stabilize the selected cathode pressure (differential pressure) and temperature at the selected current density. Carry out the BoT polarisation curve as defined above in descending mode Monitor H₂ concentration and decrease pressure at low current densities if needed (if H₂ in O₂ >3%)
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	<ul style="list-style-type: none"> • Carry out BoT AC-impedance spectroscopy • Carry out a durability test of 1000 h at 5 A cm⁻² • Carry out EoT polarisation, AC-impedance spectroscopy and eventually cyclic voltammetry for the anode. • Report data as Potential (V) vs. Time (h) along with temperature, pressure and catalysts loadings. • Determine average voltage increase from best fitting procedure • Compare EoT polarisation curves and AC-impedance spectra. Compare EoT CV with the one recorded on a similar cell at the BoT. • Determine performance and efficiency decrease at the nominal current density, surface area, series and polarisation resistance changes
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METRIC	FREQUENCY	TARGET
MEA stability	2000 h test steady-state	Degradation <5 μV h ⁻¹ cell ⁻¹ in a 1000 h test, 5 A cm ⁻² , at 90 °C with PGM loading < 0.5 mg cm ⁻² ;
Gas cross-over	2000 h test steady-state	<2 vol % H ₂ in the O ₂ at all loads; Quote temperature, pressure and current density, alongside values

Evaluation of dynamic operation:

The following protocols are applied to assess the capability of dynamic and transient operation.

Assessment of cell dynamic behavior

Single cell dynamic performance study	MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks
Test Method: <i>Single cell assessment of the dynamic behavior</i>	<ul style="list-style-type: none"> • Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of 4 g min⁻¹ cm⁻² (water resistivity : ρ > 5 MOhm cm) • Set thermostat to desired temperature • Set pressure as required; reduce pressure until safe conditions are reached if H₂ concentration in O₂ increases above 3% • Cell conditioning: apply a load of 1 A cm⁻² for 100 hours at ambient pressure • Set cut-off voltage to 2.4 V

	<ul style="list-style-type: none"> • Carry out the BoT polarisation curve, AC-impedance spectroscopy as defined above; monitor H₂ concentration in O₂ • Followed by a 6 step cycle: <ul style="list-style-type: none"> - Step 1: 10 seconds at 1 A cm⁻² (20% load) - Step 2: 10 seconds at 5 A cm⁻² (100% load) - Repeat this test 500 times to form a first set of accelerated stress test - AST • Carry out control polarisation, AC-impedance spectroscopy • Report data as Potential (V) vs. Time (h) along with current density, temperature, pressure, and catalysts loadings. • Determine average voltage increase from best fitting procedure • Compare polarisation curves, AC-impedance spectra and EoT CV with those recorded on the same cell or a similar cell at the BoT. • Determine performance and efficiency decrease at the nominal current density, surface area, series and polarisation resistance changes
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4 Definition of a set of protocols and data treatment for assessing PEM Electrolysis Stacks under high pressure and high temperature operation

1.2.2 Stack performance

The following procedures deal with water electrolysis stack validation in terms of performance and stability. Stack assembling is carried out according to the optimized procedure derived in AVANCEPEM. Stack testing is carried out under controlled temperature and pressure conditions with a tailored balance-of-plant. Stack performance is assessed by polarisation curves at the beginning of the test. The protocol is like that of the MEA assessment in a single cell. For the stack, the data analysis includes the distribution of the recorded voltages among the different cells. Results are interpreted in comparison to the single cell MEA assessment and taking the stack design into account.

Performance:

Assessment of stack performance

Stack polarisation curve Stack assembling according to the project fabrication procedures and related checks

Test Method: <i>Performance assessment</i>	<ul style="list-style-type: none"> • Feed anode manifold with water at a rate of 4 g min⁻¹ cm⁻² of total area (water resistivity: $\rho > 5$ MOhm cm) • Set water thermostat temperature at 30 °C • Set cut-off voltage to 2.4 V cell⁻¹
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	<ul style="list-style-type: none"> • Cell conditioning: apply a load of 0.2 A cm⁻² for 24 hours to favor membrane hydration, in-situ purification, and stabilisation of the anode catalyst oxidation state. • Stabilize the selected cathode pressure (differential pressure) and outlet water temperature at the maximum current density. Use a thermostat to manage for isothermal operation in combination with maximum current density. • Carry out the overall stack polarisation curve as defined in the MEA chapter in descending mode. Monitor both overall stack voltage and individual cell voltages. • Monitor H₂ concentration in oxygen at each current density • Decrease pressure at low current densities if needed (H₂ in O₂ >3%) • Repeat polarisation curve in ascending mode to check for hysteresis. • Carry out AC-impedance spectroscopy of cells and overall stack by modulating the load (e.g., using Gamry instrumentation). • Repeat tests at various temperatures (30 - 140 °C) and pressures (ambient - 20 MPa); for operation above 90 °C minimum pressure at both anode and cathode is 5 bar_{abs}. • Report data as Stack Potential (V) vs. Current density (A cm⁻²) and Average Cell Voltage (V) vs. Current density (A cm⁻²) along with temperature, pressure and catalysts loadings. • Report histograms for individual cell voltages at selected current densities • Report AC-impedance spectra of the overall stack and selected individual cells. The reported cell temperature is the water temperature at the anode outlet.
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METRIC	FREQUENCY	TARGET
Stack performance	BoT	>5 A cm ⁻² at 1.85 V cell ⁻¹ at T>90 °C with PGM loading <0.5 mg cm ⁻² ;
Gas cross-over	BoT-EoT	<2 vol % H ₂ in the O ₂ at all loads; Quote temperature, pressure and current density, alongside values

1.2.3 Stack stability

Assessment of stack stability

Stack durability study	Stack assembling according to the project fabrication procedures and related checks
Test Method: <i>Stability assessment</i>	<ul style="list-style-type: none"> • Safety conditions as reported for the polarisation measurements. • Feed anode with water at a rate of $4 \text{ g min}^{-1} \text{ cm}^{-2}$ of total area (water resistivity; $\rho > 5 \text{ MOhm cm}$) • Set cut-off voltage to 2.4 V to cover the full range • Set thermostat temperature at the desired value • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours. Pressure setting to the intended test pressure. • Stabilize the selected cathode pressure (differential pressure) and water outlet temperature, at the anode compartment, at the selected current density. • Carry out the BoT polarisation curve as defined above in descending mode • Monitor H_2 concentration and decrease pressure at low current densities if needed (H_2 in $\text{O}_2 > 3\%$) • Carry out BoT AC-impedance spectroscopy • Carry out a durability test of 1000 h at 5 A cm^{-2} • Carry out EoT polarisation, AC-impedance spectroscopy, and cyclic voltammetry • Report data as Stack Potential (V) vs. Time (h) along with temperature, pressure and catalysts loadings. Report cells voltages for the individual cells vs. time. • Determine average cell voltage increase from best fitting procedure • Compare polarisation curves, AC-impedance spectra at the BoT and EoT. • Determine performance and efficiency decrease at the nominal current density, any series and polarisation resistance changes

METRIC	FREQUENCY	TARGET
Stack stability	1000 h test steady-state	Degradation $< 5 \mu\text{V h}^{-1} \text{ cell}^{-1}$ in a 1000 h test, 5 A cm^{-2} , with PGM loading $< 0.5 \text{ mg cm}^{-2}$.
Gas cross-over	1000 h test steady-state	$< 2 \text{ vol } \% \text{ H}_2$ in the O_2 at all loads; Quote temperature, pressure and current density, alongside values

1.2.4 Stack dynamic behavior

The stack partial load behavior is assessed in combination with the balance of plant in the electrolysis system. The following protocol deals with partial load. On-off cycles are assessed with a similar approach. The main difference is that the pressure will be reduced to ambient pressure before the shut-down procedure is carried out. During start-up, the stack is pressurized at the nominal current density.

Assessment of stack dynamic behavior:

Stack partial load operation	Stack assembling according to the project fabrication procedures and related checks
Test Method: <i>Stack assessment of the dynamic behavior</i>	<ul style="list-style-type: none"> • Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of $4 \text{ g min}^{-1} \text{ cm}^{-2}$ (water.: $\rho > 5 \text{ MOhm cm}$) • Set thermostat to desired temperature • Set pressure as required; reduce pressure until safe conditions are reached if H_2 concentration in oxygen increases above 3% • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours at ambient pressure • Set cut-off voltage to 2.4 V • Carry out the BoT polarisation curve, AC-impedance spectroscopy as defined above; monitor H_2 concentration in O_2 • Followed by a step cycle for the selected time span: <ul style="list-style-type: none"> - Step 1: 10 seconds at 1 A cm^{-2} (20% load) - Step 2: 10 seconds at 5 A cm^{-2} (100% load) - • Carry out EoT polarisation, AC-impedance spectroscopy. • Report data as Potential (V) vs. Time (h) along with current density, temperature, pressure and catalysts loadings. • Determine average voltage increase from best fitting procedure • Compare polarisation curves, AC-impedance spectra with those recorded on the same cell or a similar cell at the BoT. • Determine performance and efficiency decrease at the nominal current density, surface area, series and polarisation resistance changes

METRIC	FREQUENCY	TARGET
Stack stability	1000 cycles	Degradation $< 5 \mu\text{V hr}^{-1} \text{ cell}^{-1}$, at $90 \text{ }^\circ\text{C}$ with PGM loading $< 0.5 \text{ mg cm}^{-2}$

1.2.5 Stack failure analysis

Stack diagnostics are carried out in real time during operation by monitoring specific cells (e.g., terminal cells, middle position cells) and/or groups of cells. When the stack voltage reaches the pre-set cut-off voltage (EoL) and no re-conditioning procedure is able to recover the initial performance, a stack failure analysis should be carried out. Electrochemical diagnostics such as AC-impedance analyses should be used to determine series resistance, polarization resistance for different cells in the stack. The protocols defined above for the single cell should be applied to the stack. This will need using proper electrochemical set-up for diagnostic purposes. AC-impedance is carried out preferably in galvanostatic mode by modulating the load according to the procedure described for the MEAs. Galvanostatic mode is the recommended option when the AC-impedance spectra are obtained under specific load, e.g., at 5 A cm⁻². In this case the electric power supply is modulated by an oscillator e.g., a Gamry instrument. A conventional potentiostat/galvanostat equipped with a proper current booster can be used for measuring AC-impedance spectra of specific cells in the stack in potentiostatic mode at OCV or low cell voltages e.g., 1.5 V. The ohmic resistance is determined from series resistance in the AC-impedance spectra (high frequency intercept on the x-axis of the Nyquist plot), whereas polarization resistance is determined from the difference between the low and high frequency intercepts. In the potentiostatic mode, the cell voltage is set at 1.5 V cell⁻¹ to compare the data-set to that obtained in single cell MEA testing. The frequency range should be as close as possible to the one selected for single cell MEA testing (see above).

Protocols for *in-situ* cross-over measurements of gases under practical operation include sensor methods and GC methods (H₂). Details of these operating procedures are reported in the MEA testing section.

Protocols for determining fluoride ion release are based on the use of a fluoride sensitive electrode, pH meter. Water is analysed at both anode and cathode outlet.

A post-operation physico-chemical analysis can be carried out on active (membrane, catalysts, MEAs) components to individuate any degradation effect related to stack operation. Pre- and post-operation physico-chemical analyses of active components are carried out by XRD (structural), XRF (elemental), TEM and SEM-EDX (morphological), XPS (surface analysis). The methodology is discussed above.

5 Electrolysis system validation in an industrially relevant environment

5.1 Protocols for assessing the electrolysis system under nominal operation and dynamic operating conditions

5.1.1 Operational capacity

The electrolysis system is composed by the electrolysis stack and the balance-of-plant (BoP) components. These include water and electrical supply, water drain, hydrogen and oxygen separators from water, hydrogen purification section including cooling, desiccant bed - drying units, sensors, power management, safety and control system integrated into a single and compact device. The achievement of good performance and stability as well as appropriate dynamic behavior for the PEM electrolysis system requires that all these sub-systems operate in an optimised mode.

In the system, the capacity is regulated by an electronic control system and the pressure on the output tubes.

Care is addressed to the optimization of the on-line ion exchange cartridges to reduce the trace of metal ions that can be present in the water circuit deriving from degradation of novel hardware components and the H₂-water separation. Studies carried out at short stack level concerning the

effects of water contaminants form the basis for the optimization of the ion exchange cartridges for the system.

The power conditioning/controls unit is the component of the electrolysis system that address grid fluctuations but also the other sub-units must be designed to support the dynamic behavior. An example is regarding the ion exchange resin, which needs to sustain an increase of the water temperature at the stack outlet during operation.

The system is first assessed under stationary conditions to verify if it can reach the targets in terms of performance, efficiency, stability associated to the ADVANCEPEM objectives and milestones.

Validation of nominal hydrogen production capacity and system efficiency

System operation under stationary conditions Protocol and Metrics

Operational capacity range	<ul style="list-style-type: none"> Nominal capacity: 24 kg H₂ day⁻¹ 	
System Conditioning	Operate the system at ~30% of nominal capacity and for sufficient time (24 hours) to guarantee appropriate stack/sub-systems conditioning.	
Test Conditions	System of nominal capacity <ol style="list-style-type: none"> Operate the system with a constant electric power input of 50 kW and nominal temperature and pressure for 100 hours (steady-state) Determine the average hydrogen production rate Shut-off the system 	
Number of Cycles	Set as required	
Temperature	Set as required	
Pressure	Set as required	
METRIC	FREQUENCY	TARGET
Hydrogen production rate	BoT and EoT	>24 kg H ₂ day ⁻¹ at 50kW
Energy consumption / Efficiency	BoT and EoT	<50 kWh kg ⁻¹ H ₂ or >78 % vs. HHV at 24 kg H ₂ day ⁻¹
Hydrogen quality	BoT and EoT	5 N

The system efficiency related to the hydrogen High Heating Value (HHV) at the operating temperature and pressure is defined as the ratio between the hydrogen production rate, \dot{n}_{H_2} expressed in moles per hour multiplied by the HHV expressed in Wh per mole and the electrical power supplied, P_{AC} expressed in Watt.

$$\eta^{HHV}_{system\%} = [(HHV_{H_2} \cdot \dot{n}_{H_2}) / P_{AC, system}] \cdot 100$$

The PEM electrolysis system is tested with constant 50 kW power input for 100 hours. Hydrogen production capacity, efficiency related to HHV H₂ and energy consumption per kg H₂ of produced hydrogen are determined and reported. (MS5)

5.1.2 Start-up and ramp rates and field-tests

Grid-connected electrolyzers can provide grid-balancing service provided they can operate on a wide dynamic range of operational capacity and have dynamic characteristics that address instabilities inherently

related to renewable energy thus contributing to the power regulation and stabilisation of the grid. The dynamic behavior in particular comprises fast response, cold start (BoP off), warm start (BoP on), ramp rates (BoP on) The operating mode should be electrical load following with power input up to reach the targeted H₂ production.

The protocols are addressed to validate the system characteristics to allow time-response of less than a few seconds for a change from 20 to 100% of full operational capacity and to increase the coupling efficiency of the PEM electrolyser with the grid. A wide dynamic range of operational capacity (20-100%) allows an appropriate coupling of the system with a large variation of input power or gas output requirements as it occurs with grids distributing wind and solar energy.

Start-up and ramp rates

The system is assessed to verify if it can reach the ADVANCEPEM targets in terms of fast response. This is an important characteristic for grid-service since the system must operate in response to a surplus of renewable energy fed to the grid.

The following test is addressed to assess the PEM electrolyser cold and warm start-up.

Validation of fast response (warm and cold start up)

System operation under stationary conditions

Protocol and Metrics

System Conditioning	Operate the system at ~50% of nominal capacity and for sufficient time (4 hrs) to guarantee appropriate stack/sub-systems conditioning.	
Test Conditions	System of nominal capacity	
	<ol style="list-style-type: none"> 1. Before starting test, operate the system at constant electric power input of 50 kW and nominal temperature and pressure for 24 hrs (steady-state) 2. Proceed with complete Shut-down of the system for 24 hrs (Appendix B) 3. Start-up the system in a <i>step-change</i> from 0 to 50 kW input power (e.g. 5 kW per step, with dwell time: 10 min) 4. Reduce input power from 50 kW to 10 kW in a <i>step-change</i> and keep the system under steady state for 1 hr 5. Followed by a <i>step-change</i> to 50 kW and operate at this power under steady-state for 1 hr. 6. Followed by a <i>step-change</i> to 10 kW and operate at this power under steady-state for 1 hr. 7. Record variation of electrical properties and H₂ production rate vs. time during all steps and report. 8. Shut-down the system 	
Number of Cycles	Set as required	
Temperature	Set as required	
Pressure	Set as required	
METRIC	FREQUENCY	TARGET
Rapid cold start capability.		<2 min from 0 to 50 kW
Rapid ramp-up/ramp down operation		<2-8 seconds from 20% to 100% load (10 to 50kW)
Hydrogen production rate	BoT and EoT	>24 kg H ₂ day ⁻¹ at 50 kW
Energy consumption / Efficiency	BoT Following 1 cycle	<50 kWh kg ⁻¹ H ₂ or >78% vs. HHV at 24 kg H ₂ day ⁻¹

Performance loss	After specific steps	Low decrease in hydrogen production rate (<0.01% H ₂ day ⁻¹ at 50 kW)
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FIELD TESTS

The PEM electrolysis system is thereafter tested at RWE's Innovation Centre at Niederaussem under continuous or eventually under intermittent operation. The power load profile characteristics from the grid, the hydrogen production rate and hydrogen quality are monitored and reported (**MS9-MS10**).

System duty cycles Protocol and Metrics		
Test bench preparation	<ul style="list-style-type: none"> Determine the current profile useful for a specific industrial application (duty cycle) Transfer this profile to a function generator set-up of the power conditioning/controls unit of the electrolysis system 	
System Conditioning	Operate the system at ~50% of nominal capacity and for sufficient time (4 hrs) to guarantee appropriate stack/sub-systems conditioning.	
Test Conditions	System of nominal capacity <ol style="list-style-type: none"> Before starting test, operate the system at constant power input of 50 kW and nominal temperature and pressure for 24 hrs (steady-state) Determine the average hydrogen production rate Followed by a duty cycle (24 hrs) according to the selected power profile . During the project running period, according to the G.A. , a dedicated test of the system's capability to follow the load profile of intermittent renewable power generation will be defined by RWE-G. This will be based on a realistic PV profile.	
Number of Cycles	Selected based on the application	
Temperature	Set as required	
Pressure	Set as required	
METRIC	FREQUENCY	TARGET
Hydrogen production rate	BoT and EoT	>24 kg H ₂ day ⁻¹ at 50 kW
Energy consumption / Efficiency	BoT Following 4 cycles	<50 kWh kg ⁻¹ H ₂ or >78 % vs. HHV at 24 kg H ₂ day ⁻¹
Performance loss	After specific steps Following 4 cycles	Low decrease in hydrogen production rate in line with steady-state tests (<0.01% day ⁻¹ at 50 kW)

6 Aspects related to safety issues

To ensure that the electrolytic generation of hydrogen is performed safely a short overview of the most important safety aspects that need to be considered when developing a PEM electrolyser has been preliminarily given in D7.1 and will be further implemented in D7.2.

As well known, hydrogen is prone to leaking. Combining with its low-energy ignition, wide range of combustible fuel-air mix ratios and its ability to embrittle metals means extra caution needs to be taken and the environment always monitored. Plastic or elastomeric materials used within classified areas must be antistatic. All classified areas should have both low and high oxygen sensors and hydrogen sensors.

All materials used in the electrolyser must be suitable for the range of temperatures and pressures to which the electrolyser is subjected. The materials used in the electrolyser must be stable towards hydrogen and/or oxygen, degradation caused by fluids within the electrolyser, wear resistance, and galvanic corrosion. Sampling of liquids or gases demand that precautions be taken in the design of the take-off points, which must be clearly marked.

Pressure relief valves must be used on pressurized systems. In the event of the release of hydrogen through a pressure relief valve, the electrolyser system must automatically shut down, and the relieved gas(es) must be vented into a classified area.

The lower explosion limit of hydrogen in oxygen or air is 4% (by volume). For safety, gas mixtures must maintain <2% volume fraction of hydrogen within the oxygen compartment. Both passive and active means can be used to ensure this protective level is adhered to.

The polymer electrolyte must be chemically stable over the operating conditions of the electrolyser. It must not release any chemicals nor catalyse unwanted reactions that contaminate the product gases of hydrogen or oxygen. Membrane failure can result in an explosive mixture of gases; therefore, all electrolyser devices need to include means to monitor membrane instability.

The oxygen evolution reaction puts further demands on the system. When pressurised oxygen is present, some materials have a dramatically lowered auto-ignition temperature. Any materials in contact with oxygen should have an auto-ignition temperature at least 50°C above the maximum operating temperature of the stack.

All staff present in classified areas must receive education on hydrogen safety.

7 Implementation of the EU harmonised test protocols for water electrolysis application in ADVANCEPEM

The aim of this deliverable is to define a set of protocols that comply with the electrolysis testing protocol by JRC (EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS) and extends the operating conditions to address the targets and characteristics of AVANCEPEM.

Regarding the harmonisation of the protocols and testing procedures, we have referred to the EU HARMONISED TEST PROTOCOLS led by JRC. We have not excluded similar reports by other organisations e.g., the International Energy Agency, and have considered the KPIs of the CLEAN HYDROGEN JU SRIA. Assessing PEM electrolysers according to these procedures will provide a useful basis for comparison within the CLEAN HYDROGEN JU program.

The document by JRC harmonises testing protocols and procedures for assessing electrolysers with respect to the KPIs defined in the SRIA. These protocols are useful to provide a fair comparison of results and achievements between different organisations and programs. Presently, it was necessary to establish further protocols to meet the technical specifications of ADVANCEPEM. As an example, the efficiency and performance targets in single cell are defined at 5 A cm⁻² in ADVANCEPEM. This requires data acquisition for the polarisation curves at higher current ranges than defined in the EU harmonised set of protocols.

7.1 Key-Performance Indicators

Key-performance indicators regard performance, efficiency, stability, dynamic behavior. It is important to harmonise these parameters to favor comparison of results achieved in different projects.

7.1.1 Performance

In the *EU harmonised set of protocols*, the performance of the water electrolysis process is assessed from polarization curve measurements in galvanostatic mode. Additional tests regard AC-impedance measurements and hydrogen cross-over. The approach is essentially the same discussed in ADVANCEPEM internal protocols. Polarisation curves are recorded in both increasing and decreasing current mode to assess hysteresis.

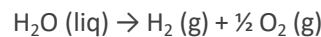
7.1.2 Efficiency

➤ Energy consumption:

In the *EU harmonised set of protocols*, the energy consumption of the water electrolysis process per unit of H₂ mass is mainly expressed in kWh kg⁻¹ H₂. This is in line with the definition given in the *ADVANCEPEM internal protocols*. At the system level, it is taken into consideration the energy consumption of all ancillary equipment used in the electrolysis system.

➤ Energy efficiency:

Since liquid water is fed to the electrolysis device, HHV values are used to determine efficiency for:



Energy (Voltage) efficiency of an electrolysis cell is determined from the ratio:

$\varepsilon_V = W_t/W_r = E_{\text{thermoneutral}}/E_{\text{cell}}$; where W_t corresponds to the actual amount of energy; W_r is the energy required to split one mole of water;

$W_r = (E_{\text{cell}} \cdot I \cdot t)$, E_{cell} is the voltage in Volt applied to the cell, I is the current in A and t is the duration in seconds.

W_t is associated to the thermo-neutral voltage, $E_{\text{thermoneutral}}$ or $E_{\Delta H}$: $W_{t,\Delta H} = (E_{\Delta H} \cdot I \cdot t)$

The thermo-neutral potential, $E_{\text{thermoneutral}}$ at standard conditions is 1.48 V.

These definitions are essentially equivalent in the *EU harmonised set of protocols* and in the *ADVANCEPEM internal protocols*.

The above definitions presume 100% Faradaic efficiency; in other words, all the DC current supplied to the stack is assumed to be converted into hydrogen. Of course, this is not the case of practical systems since there is some hydrogen cross-over and a direct recombination process may occur inside the system.

Thus, the voltage efficiency should be multiplied by the current efficiency to get the actual total efficiency of the cell This is also agreed in the harmonised EU protocols. Thus:

$$\varepsilon = \varepsilon_V \cdot \varepsilon_I$$

General formula used for determination of energy efficiency in stacks and system (that also take into account faradaic efficiency and energy consumption from the auxiliaries) are the following:

$$\eta_{\text{cell/stack}}^{\text{HHV}} = \frac{\text{HHV}}{P_{\text{cell/stack}}} \cdot \dot{n}_{\text{H}_2} \cdot 100 \%. \quad \eta_{\text{system}}^{\text{HHV}} = \frac{\text{HHV}}{P_{\text{extern}}} \cdot \dot{n}_{\text{H}_2} \cdot 100 \%.$$

The cell / stack efficiency for the Higher Heating Value (HHV) of hydrogen at the Reference operation temperature and pressure is defined as the ratio between the flow rate of the produced hydrogen, $\dot{n}H_2$ expressed in mole per hour multiplied by the hydrogen HHV expressed in Wh per mole and the electrical DC power supplied, P expressed in Watt.

System efficiency for the HHV is defined as the ratio between the flow rate of the produced hydrogen, $\dot{n}H_2$ expressed in mole per hour multiplied by the HHV expressed in Wh per mole and the total electric power provided to the system expressed in Watt.

7.1.3 Stability

➤ Average voltage degradation

The *EU harmonised set of protocols* draft reports: Average cell voltage degradation is the voltage increase per hour recorded during the test of 1000 hrs at set current of 5 A cm⁻² excluding the first 100 hrs of conditioning and considering only the time range where the cell potential continuously increases with time. The definition aims to avoid that the degradation rate is affected by a negative cell voltage trend due to cell conditioning after a start procedure.

In ADVANCEPEM the procedure for assessing durability is reported in the following:

The absolute rate of decay of performance is reported in terms of voltage increase per hour ($\mu\text{V h}^{-1}$) at constant current density. This is determined using the best fit of the curve of cell or stack voltage over time. The first 100 hrs are excluded from this analysis. In the first conditioning phase, the voltage change over time could be negative since initialization may improve cell performance e.g., seen as in Ir_(metal) anodes where the decline of voltage over time can persist for thousands of hours.

7.2 Stressor tests effects

The EU Harmonised Reference Operating Conditions for PEM water Electrolysis for Single Cell and Stack Testing are implemented in the above tables in accordance with the Grant Agreement. Deviations from the standard operating conditions may result in change of performance and durability. Both higher and lower variations from the reference operating conditions are Stressors.

Low and High Values of Stressor Conditions are set in the *EU harmonised set of protocols*. These are adopted in ADVANCEPEM. It is emphasized that the operating range defined in ADVANCEPEM extends beyond the stressor range specified in the *EU harmonised set of protocols*. A maximum temperature of 140 °C under pressure as well as a maximum operating pressure of 20 MPa are considered.

Upon application of a stressor e.g., temperature, a normalised performance is defined as follows:

$$\text{normalised performance output} = 1 - \frac{\text{voltage output under stressor conditions}}{\text{voltage output under reference conditions}}$$

Normalised performance output equal to zero means no change in performance. When the stressor causes performance reduction the normalized performance output is negative. If the stressor increases the performance, the normalized performance output is positive.

It is noted that these stressor tests provide information on current state performance only. They do not consider durability, which is an equally important factor.

8 Conclusions

The protocols and procedures defined in this deliverable are intended as means of verification to assess the achievements of the project milestones, in particular the targeted hydrogen production rate, efficiency, operating temperature, pressure and the capability of the system to operate in an industrial environment. The procedures comprise validation of optimised and scaled-up active components, MEAs, stack and PEM electrolysis systems. These procedures will provide a systematic approach to test materials, components, and systems to validate them for PEM electrolysis application.

The aim is to assess components and sub-system devices to deconvolute the properties of each component. This can allow identification of drawbacks on sub-component interfaces and can guide development towards the best integration of all the represented technologies. The aim is also to compare stack and single cell performance, to assess energy consumption at the nominal production capacity, and to establish a set of protocols for assessing performance degradation in terms of terminal voltage increase in steady-state tests and duty cycle experiments.

Finally, these protocols can be viewed as a draft to expand the harmonized testing regime for PEM electrolysis systems in anticipation that more systems with similar technical characteristics will be developed outside ADVANCEPEM.

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