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DELIVERABLE REPORT

D2.1 – Harmonised test protocols for assessing system components, stack and balance of plant in a wide range of operating temperature and pressures		
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Authors	A.S. Aricò, S. Siracusano, N. Briguglio, S. Trocino, V. Baglio (CNR-ITAE) D. Greenhalgh (ITM) S. Hody (ENGIE) C. Oldani, S. Tonella, M. Infantino (SOLVAY) L. Grahl-Madsen (EWII)	
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R	*Report*	*X*
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SUMMARY	
Keywords	*Electrolysis, Polymer electrolyte membranes, Electro-Catalysts, MEAs, Characterisation, Stack, System, Balance-of-plant, Procedures, Protocols*
Abstract	The objectives of this deliverable are to define characterisation and testing protocols for the assessment of performance, efficiency and durability of PEM electrolyser components, stack and balance-of-plant developed in the project to address wide operating conditions in terms of operating current density, temperature and pressure. The procedures and methods defined within are a set of protocols for ex-situ and in-situ characterisation of active components such as membranes, catalysts, and electrode-membrane assemblies (MEAs). Included are steady-state and accelerated durability tests as well as performance evaluation under specific operating conditions. These test protocols are also addressed to the assessment of performance, efficiency and durability of a PEM water electrolyser (PEMWE) stack operating under high current density (up to 8 A cm^{-2}), high temperature (up to 140 °C) and high pressure (up to 100 bar). For operation under such extreme conditions, the stack has to be surrounded by a specifically designed balance of plant. Accordingly, specific procedures are regarding an evaluation of the overall PEM electrolysis system under the operating conditions targeted within the project. The procedures essentially include polarization curves, differential pressure operation, gas crossover analysis and durability tests. A protocol for stack failure analysis is formulated and the aspects related to safety issues are also discussed. For what concerns the balance of plant, particular efforts are addressed to assess the dynamic behaviour of such advanced electrolyser. Specific protocols regard load and on-off cycles, assessment of the dynamic performance using specific current profiles simulating intermittent operation. In parallel, the aim of this activity is also to implement the harmonised characterisation protocols developed by the Joint Research Laboratory of the European Commission (JRC-IET) for testing MEAs & stacks with an extension of operating conditions to address the specific NEPTUNE project targets. The definition of these protocols will serve as an input for both the harmonization efforts within the FCH JU program but also to provide input to subsequent specification work as well as to enable planning of the test activities in WP3, WP4, WP5 and WP6. The specific procedures are thus addressed to: - Mapping of system level requirements to component level requirements -Define a set of protocols for assessing the PEM electrolysis system under stationary conditions in terms of performance, efficiency & durability. - Define a set of procedures for the assessment of PEM electrolyser system in relation to the operation under specific duty cycles.
Public abstract for confidential deliverables	*N.A. - Public Deliverable*

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D2.1 – HARMONISED TEST PROTOCOLS FOR ASSESSING SYSTEM COMPONENTS, STACK AND BALANCE OF PLANT IN A WIDE RANGE OF OPERATING TEMPERATURE AND PRESSURES

SUMMARY

1. INTRODUCTION

In general, the protocols reported in this deliverable describe a set of characterisations for system components including BoP, full stacks, membranes, catalysts and MEAs for operation under project relevant conditions. Specific attention is addressed to align internal procedures with the specific test protocols and parameters from the set of harmonised Joint Research Laboratory of the European Commission (JRC-IET) characterisation procedures for water electrolysis.

The relevance of the present protocols is primarily to screen the best performing membranes, anode and cathode catalysts, as well as MEAs, prepared by using different methods, to address extreme conditions and secondarily to allow for a comparison of the results achieved in different laboratories. Implementation of the harmonised procedures in the project will allow validating the quantitative project targets in terms of performance, durability and dynamic behaviour in a wider range of current densities, temperature and pressures than those indicated as stress conditions (stressors) in the harmonised document from JRC.

The present collaboration with the Joint Research Laboratory of the European Commission, initiated in previous FCH JU projects for harmonisation of specifications and protocols, will continue and be further strengthened within the NEPTUNE project.
Such collaboration consists in providing information to JRC about the set of protocols and procedures used in NEPTUNE as well as supplying information on the safety aspects for the advanced high temperature, high pressure electrolysis technology in order to allow JRC considering an extension of the set of operating conditions in their analysis. It is planned within NEPTUNE that any safety-related event that may occur during the execution of the project will be reported to the European Commission's Joint Research Centre (JRC), which manages the European hydrogen safety reference database, HIAD.

It is important to point out that a harmonised set of test protocols, when produced by a group of several stakeholders, may result in a number of compromises between the different requirements of the various programs which are carried out. Accordingly, the harmonised protocols, although extremely useful to provide a fair comparison of the results and achievements within the different organisations and programs, may not completely adapt to the specifications of a particular project especially when this is addressing extreme operating conditions such as NEPTUNE. Thus, based on the specific requirements of the NEPTUNE project, it was preferred to delineate for some Key Performance Indicators (KPIs), two sets of protocols. One is for specific use internal to the NEPTUNE project and another parallel set of protocols is derived from the specific document on harmonised electrolysis procedures produced by JRC (EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS). The same applies to the definition of the specific set of parameters e.g. efficiency definition. When more than one way of defining a parameter is provided in the TERMINOLOGY document produced by JRC, a specific selection is made within NEPTUNE together with a proper explanation about the choice made.

As discussed, an important approach consists in using the procedures defined in the JRC harmonisation documents but extending these to the extreme operation conditions of NEPTUNE. In general, the internal protocols are aiming to assess the achievement of project milestones as indicated in the Description of Work of NEPTUNE.
When the internal procedures differ consistently from the harmonised procedures led by JRC, experiments carried out according to both sets of protocols can thus give an indication if the achievements of a specific milestone or project objective is sensitive to the particular method used. It is in any case

important to assess the achievement of the most relevant parameters according to the set of harmonised protocols from JRC. This should be hopefully adopted, widely, within the FCH JU program (FCH JU projects) to provide a useful basis for comparison.

The focus of this deliverable report is thus primarily on the protocols and procedures useful to assess operation of PEM electrolysis components and devices under the extreme operating conditions targeted in the NEPTUNE project. The protocols normally used to assess the PEM electrolyses components and system working under conventional operating conditions are preferably not reported in detail here since these have already been treated in public deliverable reports of previous projects, e.g. FCH JU HPEM2GAS G.A. 300081. This is unless the protocols require a specific update because the experience acquired in previous projects may suggest some changes in the testing procedure.
The previous public deliverables of HPEM2GAS, regarding testing protocols, have been published in the project website and are, in principle, available also from the European Commission Cordis web-site. The same approach will be used in NEPTUNE where these deliverables are also public with benefits for the entire electrolysis community.
The protocols reported in the next chapters to assess extreme operating conditions are still essentially based on electrochemical polarization (voltage vs. current density or j-V) curve, beginning of test (BoT) and end of test (EoT), to determine important 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. This to simulate the required behaviour for interfacing the PEM electrolyser to a renewable power source (off-grid) or for grid-connected applications (power-to-gas, grid balancing service etc.).
Some useful diagnostic analysis has been considered to understand specific stresses originated from operation under extreme conditions. These are electrochemical impedance spectroscopy (EIS), gas crossover and water analysis. These can be used for in-situ MEA diagnostics and EoT characterisation. Moreover, also ex-situ tests, performed after stack disassembly can be used to assess degradation mechanism(s) for specific stress test. This includes analysis of active MEA components i.e. electrocatalysts and membranes and protocols for non-active components assessment like bipolar plates. The stability of bipolar plates is checked after prolonged operation by measuring contact resistance measurements. Thus, where appropriate, post-operation analysis (SEM, TEM, EDX, XPS, etc) can be used in order to investigate in detail phenomena that are probably not observed under conventional working conditions.

2. DEFINITION OF A SET OF PROTOCOLS FOR ASSESSING THE ACTIVE COMPONENTS OF THE PEM ELECTROLYSIS STACK FOR OPERATION UNDER EXTREME CONDITIONS

The procedures and methods defined in this chapter are a set of protocols for ex-situ and in-situ characterisation of active components such as membranes, catalysts, and electrode-membrane assemblies (MEAs). These components form the core of a PEM water electrolyser and their properties influence the capability of the stack to operate under extreme conditions of temperature, pressure and current density.

2.1 ASSESMENT OF PEM ELECTROLYSIS MEMBRANES FOR OPERATION AT HIGH TEMPERATURE AND PRESSURE

The membrane plays a relevant role for operation at high temperature and pressure and represents the key component for addressing extreme working conditions.
It is well known that the conventional membrane used in PEM electrolysis i.e. Nafion cannot operate at temperatures above 90°C because of the low glass transition temperature. Moreover, during OCV

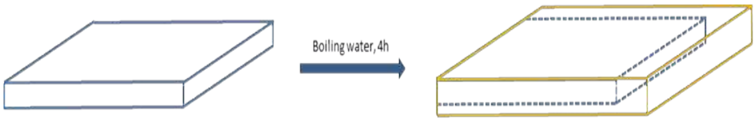
operation at low pressure (a conventional system is usually pressurised only above 0.5 A cm^{-2} current density to avoid that the hydrogen concentration at the anode may reach the flammability limit), membrane dehydration above 90 °C gives rise to a strong decrease of proton conductivity.
Operation at high current density can be only achieved by reducing the ohmic drop to avoid significant efficiency losses. This can be obtained by increasing significantly the membrane conductivity or using thin membranes. Proton conductivity is the result of proton mobility and concentration. One can increase these two factors by decreasing the equivalent weight and the size of water channels or ion clusters within the membrane. Both modifications cause a relevant increase in gas permeation and a decrease of the dimensional stability. Thus, during differential operation (pressurised hydrogen and non-pressurised oxygen), gas crossover is exacerbated by both a low thickness and low EW of membranes. Moreover, high pressure operation causes mechanical stresses on the membrane that can be properly addressed by improving mechanical properties e.g. using a reinforcement. Accordingly, proton conductivity, crossover, swelling, mechanical properties, glass transition temperature are relevant parameters for membrane operation under extreme conditions.

For what concerns the membrane characterisation, at the time of writing, there are no protocols yet designed by JRC for membrane assessment with regard to the electrolysis application. No comparison is thus reported.

2.1.1 Chemical, thermal and mechanical (dimensional) stability

Chemical and thermal stability Protocols

Membrane Conditioning	1 M H_2SO_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 and report with the result
Test Method: *Thermal Stability*	• 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. • Report weight losses corresponding to the specific temperature ranges • Associate weight losses to specific degradation processes
Test Method: Glass transition temperature	• Carry out Dynamic Mechanical Analysis (DMA) to study viscoelastic properties of the polymer electrolyte under specific applied 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, frequency 1 Hz. • Report Tg at maximum of tan(δ) • Glass transition temperature defines the maximum operating temperature of the membrane under full hydration conditions
Test Method:	• Release of fluorine species is measured as function of time during time-tests under electrolysis conditions.

Chemical and Hydrolytic Stability	• Fluoride species are determined with a 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: *Oxidative Stability*	• Samples will be cut from a larger sheet of membrane once the sheet has been hydrated • Fenton's Test – Reagents: 15% H_2O_2 (200 g), $Fe(NH_4)_2(SO4)_2*6H_2$ (0.05 g) and H_2SO_4 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, possibly, 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: *Mechanical stability*	• Apply stress-strain method ASTM D638 type V (23°C, 50% RH) with a speed 0.25 mm/min. • If applicable repeat the same test at different temperatures relevant for the specific application • Determine relevant mechanical resistance parameters (Young's modulus, stress/strain at break, yield stress/strain)
Test Method: *Dimensional swelling*	• Membrane immersion for 4 h in water at the relevant temperature in a closed glass or plastic bottle. • Rectangular samples cut from each sheet of polymer with equal numbers cut in each of 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 

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

2.1.2 Conductivity and gas crossover

Exchange capacity, water uptake and proton conductivity are interrelated parameters in perfluorosulfonic membranes. It is well known that 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 crossover. Assessment of these relevant properties are thus grouped together. Hydrogen crossover is one order of magnitude higher than oxygen crossover in proton conducting membranes. This is further exacerbated by the high differential pressure between the cathode and the anode. Thus, it is relevant measuring the hydrogen crossover since the system is operated under differential pressure with pressurised hydrogen and non-pressurised oxygen. Moreover, the hydrogen is purified at the outlet of the stack and any traces of oxygen that may permeated can be removed. Oxygen crossover has been treated in previous projects dealing with balanced pressure. Here only the hydrogen crossover protocol is treated, updated for the targeted applications. Area specific resistance (series resistance) for the membrane is determine accordingly to the membrane thickness and the intrinsic ionic conductivity. This is the parameter that directly influences ohmic drop at high current density.

Exchange capacity, Water uptake, Proton conductivity, Area specific resistance, Gas crossover Protocol and Metrics

Membrane Conditioning	1 M H_2SO_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 and report with the result
Test Method: *Membrane exchange capacity*	• Dry membrane (vacuum treatment 2 h at 105°C) is weighted. • Equilibration of > 1 g membrane in known excess ($[NaOH]_{ex}$) of 0.1 NaOH at room temperature for 4 hrs • Titration of $[NaOH]_{ex}$ with 0.1 M HCl ($[NaOH]_{tit}$) • IEC in meq/g (3 d.p.) measured by titration as difference $[NaOH]_{ex}$ - $[NaOH]_{tit}$ • Equivalent weight (EW) determined according to: 1 eq = 1 mol of SO_3H • EW measured in g/eq.
Test Method: *Membrane water Uptake*	• Soaking pre-weighed and carefully dried membranes (vacuum oven, 2 h at 105°C) in boiling water (W_{dry}). • After 4 h, equilibrated samples are rinsed in cold water, • 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: $Water\ Uptake\ (\%) = \left(\frac{W_{wet}}{W_{dry}} - 1\right) * 100$
Test Method: *Membrane Ionic Conductivity / area specific resistance*	• Measure membrane proton conductivity by Bekktech cell with bi-distilled liquid water or milliQ water. • 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 a wide range of temperatures from ambient to 140 °C, in steps of 20 °C with pressure varying from ambient pressure to 5 bar_{abs} with further steps of 10 bar. 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: $R*S=\rho*l$ where R is the high frequency resistance, S the surface area, ρ is the reciprocal of conductivity $(1/\sigma)$ and l is the thickness.
Test Method: *Ionomer dispersion*	• 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.
Test Method: *Hydrogen crossover*	• The hydrogen crossover is measured in-situ, at MEA level, under specific operating conditions of temperature and pressure as targeted in the project • This is carried out by placing a H_2 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 • Calibrated H_2 sensor (i.e. HY-OPTIMA) in-line in gas flow on O_2 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)

METRIC	**FREQUENCY**	**TARGET**
Proton conductivity		>0.2 S/cm
area specific resistance		< 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

2.2 ASSESSMENT OF PEM ELECTROLYSIS ELECTROCATALYSTS FOR OPERATION AT HIGH CURRENT DENSITY

The catalysts selected for operation in PEM electrolysis at high current density are mixed oxides of Ir and Ru oxides (anode) and Pt on carbon (cathode). The aim of NEPTUNE is to reduce the noble metal loading while keeping the performance and stability at proper levels. A good electro-catalytic activity is essentially dealing with a low overpotential at high current densities (4 A cm^{-2}) as targeted in this project whereas an enhanced stability regards both steady-state and cycled operation and can increase significantly the durability of the electrolyser.

A minimum set of protocols is defined to assess the electro-catalysts for operation under critical conditions in terms of high current density, high temperature and high pressure. The protocols are essentially dealing with the identification of the relevant physico-chemical properties, such as mean crystallite size, particle size, surface area, that influence predominantly the electrocatalytic activity, the assessment of overpotentials at 4 A cm^{-2}, the assessment of catalyst durability in MEAs with the selected ionomers and the capability of managing hydrogen crossover reduction by the recombination catalyst. The aim is to produce a data-set for identifying relevant properties of the electro-catalyst that can qualify such materials for operation under targeted conditions.

2.2.1 Physico-chemical properties

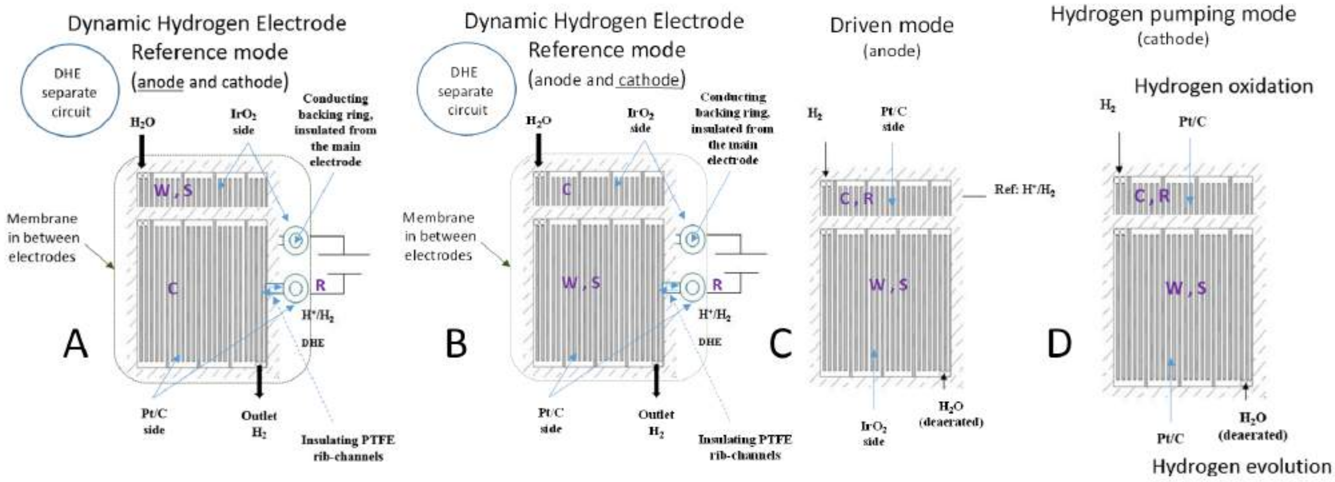
Catalysts physico-chemical properties

Anode and cathode catalyst powders	Catalysts are produced in powder form or milled to form a powder in order to allow ink preparation in combination with the ionomer for MEA fabrication.
Test Method: *Structure, alloying, crystallite size*	• Carry X-ray diffraction (XRD) to determine crystallographic structure • Determine degree of alloying from peak shift after calibration using Vergard's law • Determine mean crystallite size from peak broadening using the Debye-Scherrer method • Report mean crystallite size in nm
Test Method: *Chemical properties*	• Determine the Pt content of Pt/C catalyst from thermogravimetric analysis by burning the organic fraction at 950-1000 °C • 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: *Surface properties, core-shell structures*	• 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	< 3 nm
Mean crystallite size/particle size anode (IrRuOx)		<10 nm
Electrochemcial active surface area cathode (Pt)		>50- 80 m^2/g
Surface area anode		>100 m^2/g

2.2.2 Electrochemical properties

In-situ electrochemical assessment of anode and cathode catalyst is the preferred procedure to avoid interference and effects from the liquid electrolyte that may cause leaching, adsorption of anions etc. In situ catalyst assessment provides information about the effective catalytic activity and the catalyst-ionomer interface.
This however, requires some specific modus operandi. Three main approaches are presented here: the dynamic reference electrode mode (anode and cathode), the driven mode (anode), the hydrogen pumping mode (cathode).



Adapted from A.S. Aricò et al. Novapublisher ed. ISBN: 978-1-60876-865-3

Fig. 1 Cell configuration for in situ electrocatalyst assessment in PEM electrolysis (a serpentine flow field is here designed for convenience; it could be a circular geometry based on a different flow field design or just a metal foam).

A Dynamic Hydrogen Electrode (DHE) is used as reference electrode using a configuration similar to that reported above (A.S. Aricò et al. Novapublisher ed. ISBN: 978-1-60876-865-3). The DHE (separate circuit) could be based on two small pieces of Pt/C and IrO$_2$ electrodes contacting the membrane (the same membrane of the main electrodes) on opposite sides. These small electrodes are not in electrical contact with the main electrodes, but they are exposed to the same gas or water flows as the main electrodes trough PTFE rib channels (see figure 1 A and B). The two small pieces of Pt/C and IrO_2 electrodes forming the DHE are polarized with a very small current (e.g. a few mA cm^{-2}) to have a small H_2 evolution on the negative electrode that acts as reference DHE electrode. The small negative electrode made of Pt/C in the separate circuit is referred as DHE and used as reference (see figure 1 A and B).

In the driven mode, the Pt/C cathode is used as both reference and counter electrode whereas the Ir-Ru Oxide anode is the working (and sense) electrode (see Fig.1C). Since the hydrogen evolution/oxidation is a fast process, being the current involved in the experiment relatively low, the counter-reference electrode is not significantly polarized, and it can be referred as Reversible Hydrogen Electrode (RHE).

In the hydrogen pumping mode, Pt/C is used at both electrodes. Hydrogen is fed to one electrode and water to another electrode (see Fig.1D). The overall cell polarisation thus results from the sum of the two processes which are very similar in reaction kinetics being the hydrogen evolution/reduction process highly reversible and characterised by a high exchange current density. Thus, the overall polarisation can be split in two to get the half-cell cathode polarisation.
At the present, there are no harmonised protocols from JRC for determining the electro-catalysts properties. Thus, no comparison is possible.

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).
Test Method: *Anode polarisation using the driven mode operation*	• 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 ml/min/cm2 • 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 (Fig. 1C) 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 (Rs ≡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 4 A cm^{-2} vs. RHE, report T and P, report noble metal loading
Test Method: *Cathode polarisation using the hydrogen pumping mode*	• 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 4 A cm^{-2}. Feed water at a rate of 4 ml/min/cm2 • 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 (Fig. 1D) • 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 (Rs $\equiv$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 • Report anode overpotential at 4 A cm^{-2} vs. RHE, report T and P, report noble metal loading
Test Method: Anode and cathode polarisation using the dynamic hydrogen electrode mode	• 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/cm2, allow for full hydratation of membrane, electrodes and DHE. • Polarise cathodically 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^+/H_2) 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 flown 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 (Rs $\equiv$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}

2.2.3 Electrochemically active electro-catalyst surface area

The electrochemically active catalyst surface area can be determined in situ or ex-situ. Ex-situ is usually the preferred method by the academic community to provide an information on an intrinsic property of the catalyst under conditions that can be reproduced in all laboratories. However, using this method, the catalyst properties are not assessed under real operating conditions and the ex-situ method cannot be used as diagnostic tool. The in-situ method is preferred for cell diagnostics in order to understand catalyst degradation e.g. after prolonged operation at high current density or at high temperature by monitoring the decrease of electrochemically active surface area.

CNR has collaborated with JRC on the harmonisation of the protocols and procedures for determining the in-situ surface area by indicating preferred approaches and procedures. Although the final document from JRC is not yet released, it was considered appropriate to align on this topic the harmonised JRC protocols with the internal NEPTUNE procedures. Thus, the protocol reported here is essentially the same of the harmonised draft document from JRC. A short description of the protocol is reported here. More details can be found in the "EU Harmonised Cyclic Voltammetry Test Method for Low Temperature Water Electrolysis Single Cells" that will be released by JRC.

There is a specific interest for in–situ determination of the electrochemically active surface area (ECSA) of the electrodes in Polymer Electrolyte Membrane Water Electrolyser by using CV. It allows to in-situ study the catalyst utilization and to investigate the ionomer-catalyst interface when different ionomers are used.

The information obtained from CV measurements of a catalyst is the Electrochemical active Surface Area (ECSA) of the electro-catalyst expressed in m^2 g^{-1} or in mC cm^{-2} along with the used sweep rate. The catalyst utilisation, U_M being the ratio between the ECSA (from CV) and the total available surface area of the catalyst (m^2/g). The latter is determined by physico-chemical methods. Thus, the catalyst utilization is generally an adimensional number reflecting the extension of the catalyst-electrolyte interface and it is expressed as percentage (%).

U_M= ECSA / 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 the liquid nitrogen temperature.

In the case of a supported catalyst such as Pt/C or Pd/C, this is determined from the mean particle size, generally 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:

$MSA = 6x10^4 / (\rho \cdot d) \equiv m^2/g$

Where 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 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 IrO_2 (or IrRu oxide) OER electrode.

A flow rate of 10 ml min^{-1} cm^2 and a dew-point temperature equal to cell temperature can be used. In the driven mode, the Pt/C cathode is used as both reference and counter electrode whereas the Ir-Ru oxide anode is the working (and sense) electrode (Figure 2).

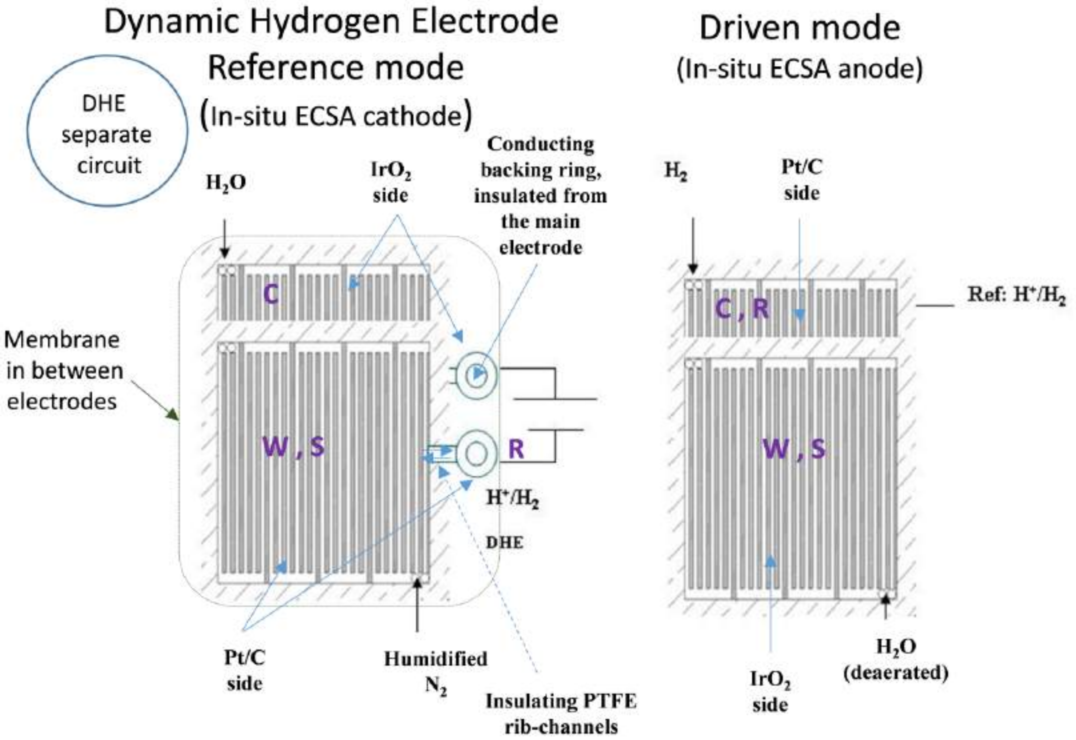


Figure 2 PEMWE configurations for the in-situ measurement of the ECSA by CV of the cathode in DHE mode and of the anode in driven mode. A serpentine flow field is here reported for convenience; it could be a circular geometry based on a different flow field design or just a metal foam (adapted from Aricò et al Novapublisher Nova Science Publishers Inc, New York (2010).

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 Reversible Hydrogen Electrode (RHE).

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

Recommended conditions are a sweep rate of 20 mV·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.

If the stoichiometry of the adsorption/desorption processes is not known for the IrO_2 (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 using a configuration similar to that reported in Figure 2.

The DHE (separate circuit) could be based on two small pieces of Pt/C and IrO_2 electrodes contacting the membrane (the same membrane of the main electrodes) on opposite sides. These small electrodes are not in electrical contact with the main electrodes, but they are exposed to the same gas or water flows as the main electrodes through PTFE (polytetrafluoroethylene) rib channels (Figure 2).

The two small pieces of Pt/C and IrO_2 electrodes forming the DHE are polarised with a very small current (e.g. a few mA cm^{-2}) to have a low hydrogen evolution on the negative electrode that acts as reference DHE electrode (Figure 2).

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 $mV \cdot s^{-1}$, 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 $\mu C\ cm^{-2}$ 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).
Test Method: Anode electrochemically active surface area using	• 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/cm2; feed cathode with 10 ml $H_2/min/cm^2$

the driven mode operation	- 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 (Fig. 2left) using the cathode as reference (RHE) and counter electrode - Determine series resistance (Rs ≡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.
Test Method: Cathode electrochemically active surface area using the DHE mode operation	- 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 (Fig. 2 right). - Feed anode with water at a rate of 4 ml/min/cm2 allow for full hydratation 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 (Fig. 2left) using the DHE cathode as reference (RHE) and the anode as counter electrode - Determine series resistance (Rs ≡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 µC cm^{-2} for one monolayer coverage for hydrogen on Pt and the measured charge determine cm^2_{real} - Roughness factor: cm^2_{real}/ cm^2_{geo} - Using cm^2_{real} and noble metal loading determine the surface area in m^2/g.

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 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

2.2.4 Degradation of electrocatalysts during operation

Durability issues are well known in the case of electrodes operating at high current density with ultra-low catalyst loadings. Large increase of degradation rate at low catalyst loading under operation at high current density is produced by the strong increase of turnover frequency. A progressive increase of the degradation rate with the turnover frequency has been reported in a recent HPEM2GAS paper [Siracusano et al Nano Energy 40 (2017) 618–632]. Catalyst operation at high turnover frequency was observed to cause a progressive change of Lewis acidity characteristics with time for both Ir and Ru cations thus influencing their ability to promote water oxidation. Assessment of catalyst degradation can be carried 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 are important diagnostic tools providing information on catalyst degradation. This information is complemented by ex-situ physicochemical study according to the procedures reported above. An example of protocol for in-situ assessment of catalyst degradation is reported below.

Assessment of electrocatalyst degradation

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).
Test Method: *In situ assessment of electrocatalyst degradation*	• 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/cm^2 for nominal operation (4 A cm-2 and 90°C). This is selected in order 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/cm^2 at 140 °C or 8 A cm-2. Set temperature and pressure as required, differential pressure is the preferred approach (during measurement %H_2 in O_2 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 4 A·cm^{-2} preceded by a 100h at 1 A·cm^{-2} for conditioning • Determined series resistance (Rs ≡Ohm cm^2) 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 4 A·cm^{-2} before and after the durability test. Report noble metal loading.
Test Method: *Ex situ assessment of electrocatalyst degradation*	• 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**
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 4 A cm^{-2} before and after a durability test of 2000 h at 4 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 4 A·cm^{-2}	

2.2.5 Recombination catalyst

An efficient and stable recombination catalyst integrated in the MEA can contribute to crossover management under high differential pressure. The protocol to assess the in-situ performance of the recombination catalyst is reported below.

Assessment of recombination catalyst	
In situ recombination catalysts assessment	Recombination catalysts is integrated in the MEA during preparation
Test Method: In situ assessment of electrocatalyst degradation	- 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/cm2 - Set temperature as required

	- Cathode pressure is varied in steps starting from the lowest pressure to the highest pressure and reverse. Maximum pressure 10MPa. - Anode pressure is set to ambient (at <90 °C) or 5 bar_{abs} (at >90 °C) and kept fixed - Carry out MEA polarization control (see MEA chapter) - Carry out steady-state operation test of at least 30 min at 4 A cm^{-2}, 3 A cm^{-2}, 2 A cm^{-2}, 1 A cm^{-2}, 0.5 A cm^{-2}, 0.2 A cm^{-2} - During these tests measure H_2 concentration in oxygen according to the methods discussed above. The microGC method is preferred vs. the hydrogen sensor because of better accuracy. - Determine H_2 concentration in oxygen at different differential pressures as function of the operating current density - Compare crossover results with those recorded for a MEA without recombination catalyst.

METRIC	**FREQUENCY**	**TARGET**
Hydrogen crossover	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

2.3 ASSESSMENT OF PEM ELECTROLYSIS MEAS FOR OPERATION UNDER EXTREME CONDITIONS

A set of measurement procedures is defined to assess the capability of the membrane-electrode assemblies developed in NEPTUNE to address extreme operating conditions and to achieve the project targets. These procedures deal with determination of mass loading of catalysts, performance, efficiency, stability, capability to sustain dynamic operation.

CNR has collaborated with JRC on the harmonisation of the protocols and procedures for measuring polarisation curves of membrane-electrode assemblies in PEM electrolysis by indicating preferred approaches and procedures. A document has been officially released by JRC. Accordingly, it was considered appropriate to align on this topic the harmonised JRC protocols with the internal NEPTUNE procedures. Thus, the protocol reported here for MEA polarisation curve is essentially similar to the harmonised document from JRC. However, operating conditions are here extended from 2 A cm^{-2} (JRC) to 8 A cm^{-2} (NEPTUNE). Also, the operating range for pressure and temperature are significantly wider in NEPTUNE (10 MPa, 140 °C). More details can be found about the polarisation curves under conventional operating condition in the document "EU Harmonised Polarisation Curve Test Method for Low Temperature Water Electrolysis" released by JRC. The protocol here discussed is thus the same of the harmonised protocol under conventional conditions while covering a much wider range in terms of temperature, pressure and current density.

2.3.3 Catalyst loading in MEAs

MEA performance, efficiency and stability strongly depend on the catalyst loading. As discussed above, there is a large increase of MEA degradation rate at low catalyst loading under operation at high current density. This is caused by the increase of the turnover frequency for the catalytic site. It is thus important to compare performance and stability of different MEAs in the presence of similar catalyst loadings. NEPTUNE projects targets refer to specific catalyst loading.

Determination of the catalyst content is carried out by weighing the MEA (membrane) before and after deposition of the catalytic layers (preceded by a step of drying in vacuum at 80°C for 30 min). This is a simple non-invasive approach that can be properly 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. Chemical analysis (e.g. X-ray fluorescence) can be eventually applied to the complete MEA even if the accuracy on high atomic weight and low atomic weight elements is significantly different using this technique.

For small area MEAs, produced in in a similar way to those used in catalyst assessment experiments, a useful approach could be to burn some of the complete MEAs of 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 and 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. Their contents are normalised to the geometrical MEA area. This can be used especially for very low catalyst contents.

2.3.4 Cell diagnostics: ac-impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements: the main objective of the recording EIS spectra is to determine the series and polarization cell resistance. EIS spectra can be recorded in potentiostatic mode starting from OCV thereafter at 1.5 V, 1.8 V and finally at the maximum achieved potential or under galvanostatic mode at 50 mA cm^{-2}, 100 mA cm^{-2}, 4 A cm^{-2} and the maximum achieved current, depending on the active geometrical electrode area under consideration. In the potentiostatic mode, the procedure consists in 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.

2.3.5 Assessment MEA performance in single cell

MEA screening is first carried out in a small single cell (<25 cm^2 geometrical area) and thereafter the optimised MEA is assessed in large area cells (>25 cm^2). The flow field design can vary substantially for the different laboratories. It could be a rectangular geometry with a serpentine flow field or a circular geometry with a foam diffusion layer for high pressure studies. This affects MEA performance. However, for internal comparison the standard 8 cm^2 design from ITM is used in all NEPTUNE partners' laboratories to allow for comparison.

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 fixed to 4 g cm^{-2} min^{-1}.

Differential pressure is the preferred operation. Reference cathode pressures are: 1 bar_{abs} for low pressure studies, 30 bar_{abs} or 100 bar_{abs} for high pressure experiments. For operation above 90°C, the anode is pressurised at 5 bar_{abs}.

Water quality: ρ> 5 MOhm cm.

MEA conditioning: MEA is installed in a single cell and equilibrated at 90°C with deionised water (ρ> 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 favour 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 hrs at 1 A cm^{-2}.

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. This is determined by the specific form of the Volmer-Butler equation, which indicates an exponential increase of current as function of the overpotential. Thus, there is the need to sample a large number of data at low current and less at high current; whereas, the trend at high currents is essentially governed by the ohmic drop and thus the linear relationship of the Ohm law. Mass transport effects with the corresponding inflection point in the polarisation curves at high current densities are less frequent in PEM electrolysis polarisation.

Sweep mode: at ambient pressure, for an initial assessment, the polarization curve is measured from lowest to the highest current density (ascending part of the polarisation curve) followed by a measurement in reverse order that is from highest to lowest current density (descending part of the polarisation curve). This will allow to assess the maximum operating current density.

Once the maximum operating current density for the specific MEA is established and for operation at high pressure, the performance is instead measured from the highest to the lowest current density (descending part of the polarisation curve) followed by a measurement in reverse order (ascending part of the polarisation curve).

Safety: The operating pressure is stabilized at the maximum current density before carrying out the polarization curve in descending mode. The H_2 concentration in the O_2 stream should be monitored by a hydrogen gas sensor at each current density to avoid reaching the flammability limit (4% H_2 in O_2).

At low current densities, especially under high differential pressure, the H_2 concentration in the oxygen stream can increase significantly approaching the flammability limit. Thus, the pressure is usually decreased when the H_2 concentration in the oxygen reaches 3% (ambient pressure operation is recommended to record polarisation curves in this low current density region.

Cut-off-voltage: The measurement should be aborted when the cell voltage is 2 V or above (cut-off voltage). Note a higher cut-off voltage, of 2.4 V may be applied when there is durability testing, or it is aimed to reach a current density of 8 A cm^{-2}.

Data collection: Variation of the current density is thus carried out in steps as reported below; the duration of each step is 1 min (pseudo steady state-condition). The average potential is reported at each current density. The change in the cell voltage for 1 min, generated by variation of current is registered in a table such as the one reported below.

The left-hand column (blue colour) matches exactly with the sampling data-set reported in the “EU Harmonised Polarisation Curve Test Method for Low Temperature Water Electrolysis” released by JRC.

The second data set (right column, red colour) is instead dealing with the extension of the current density range in NEPTUNE until the nominal current density of 4 A cm^{-2} and to the extreme limit of current density of 8 A cm^{-2}.
For the latter the cut-off voltage can be increased from 2 to 2.4 V/cell.

The isothermal condition (no relevant temperature gradient at different current densities) could be established by using a thermostat for the water recirculating. Water recirculation thus acts as a thermostating fluid. The cell temperature and pressure should be stabilised at the maximum operating current density before proceeding with the polarisation curve from the maximum current density to the open circuit voltage. In any case, the inlet water temperature must be controlled; this is used as the reference point.

If the polarisation curve is carried out with high differential pressure, the operating cathode pressure should be decreased to ambient pressure (when operating at 30 – 90 °C) or 5 bar$_{abs}$ (when operating at >90 °C), if H_2 in O_2 reaches 3%, when measuring lower current densities. The measurement of the hydrogen concentration in oxygen will indicate the pressure limit for constant pressure polarisation measurements in the presence/absence of a recombination catalyst.
Low current density can be useful in the case it is needed to determine the Tafel slope. Otherwise, the polarisation can start at 0.01 A cm^{-2}.

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	
0.4	
0.45	
0.5	
0.6	
0.7	

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	
5.5	
6.0	
6.5	
7.0	
7.5	
8.0	

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
Test Method: *Single cell performance assessment*	• Feed anode with water at a rate of 4 ml/min/cm2 (ρ> 5 MOhm cm) • Set thermostat to the desired temperature • Cell conditioning: apply a load of 0.2 A cm^{-2} for 24 hours to favour membrane hydration, in-situ purification and stabilisation of the anode catalyst oxidation state. • Fix cut-off voltage to 2 V, or 2.4 V according to the selected current density range (4 A cm^{-2}, 8 A cm^{-2}) • Stabilize the selected cathode pressure (differential pressure) and temperature at the maximum current density. Use a thermostat to manage for isothermal operation in combination with 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 O_2 >3%) • Repeat polarisation curve in ascending mode to check for hysteresis. • Carry out ac-impedance spectroscopy • Repeat tests at various temperatures (30-140 °C) and pressures (ambient to 10 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.

METRIC	FREQUENCY	TARGET
MEA performance	BoT	>4 A·cm^{-2} at 1.75 V/cell at T>90 °C with PGM loading < 0.4 mg cm^{-2}; >8 A·cm^{-2} at E_{Cell} < 2.2 V at T>90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	BoT-EoT	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

2.3.6 Assessment of MEA stability in single cell

An enhanced stability of the MEA will contribute to reducing the cell degradation rate at high current density (4 A·cm^{-2}) in order to limit the number of stack replacements in a typical electrolyser life-span. 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: *Single cell assessment*	• Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of 4 ml/min/cm2 (ρ> 5 MOhm cm) • Set thermostat to desired temperature • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours at ambient pressure • Fix cut-off voltage to 2 V, or 2.4 V according to the selected current density range (up to 4 A cm^{-2}, or 8 A cm^{-2}) • 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 H_2 concentration and decrease pressure at low current densities if needed (if H_2 in O_2 >3%) • Carry out BoT ac-impedance spectroscopy • Carry out a durability test of 2000 h at 4 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

METRIC	**FREQUENCY**	**TARGET**
MEA stability	2000 h test steady-state	Degradation <5 µV/h/cell in a 2000 h test, 4 A·cm^{-2}, at 90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	2000 h test steady-state	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

Transient and dynamic operation:

During real life operation depending on the application different cycling conditions can occur.

It may be required a transient operation of a few hours at very high current density e.g. 6 or 8 A cm^{-2} as well as under partial load. It was observed in a previous project that for power-to-gas applications it would be appropriate to test the system for on-off operation.

Two main protocols are defined below to assess the capability of dynamic and transient operation.

Assessment of MEA dynamic behaviour: Transient and partial load operation

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: Single cell assessment of the dynamic behaviour	• Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of 4 ml/min/cm2 (water.: ρ> 5 MOhm cm) • Set thermostat to desired temperature • Set pressure as required; reduce pressure until safe conditions are reached if H_2 concentration in O_2 increases above 3% • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours at ambient pressure • Fix 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 6-step cycle: - Step 1: 10 seconds at 0.2 A/cm^2 (5% load) - Step 2: 10 seconds at 4 A/cm^2 (100% load)

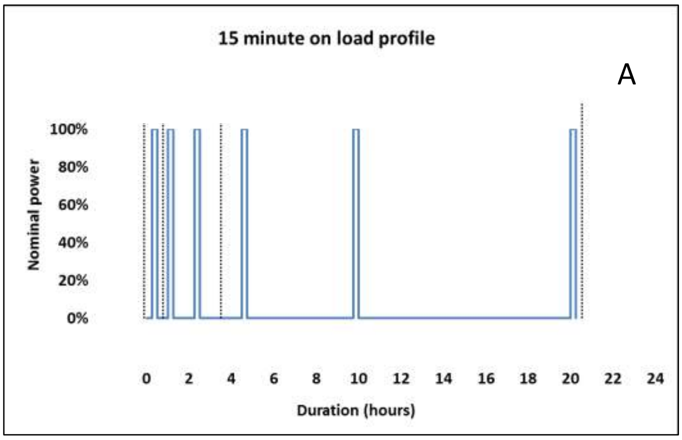
	- Step 3: 10 seconds at 6 A/cm^2 (150% load) - Step 4: 10 seconds at 8 A/cm^2 (200% load) - Step 5: 10 seconds at 6 A/cm^2 (150% load) - Step 6: 10 seconds at 4 A/cm^2 (100% load) - Repeat this test 1500 times to form a first set of accelerated stress test - AST (corresponding to ~25 h if all steps are included) • Carry out control polarisation, ac-impedance spectroscopy • Repeat AST to complete 5 sets of 1500 cycles (7500 cycles) corresponding to 125 hrs dynamic operation with 5 diagnostic intervals • Carry out EoT polarisation, ac-impedance spectroscopy and Cyclic voltammetry • 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

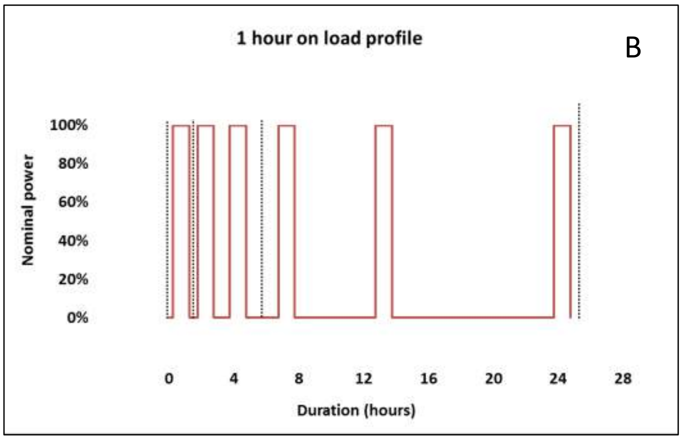
METRIC	**FREQUENCY**	**TARGET**
MEA stability	7500 cycles	Degradation <2% at 90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	7500 cycles	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bars at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

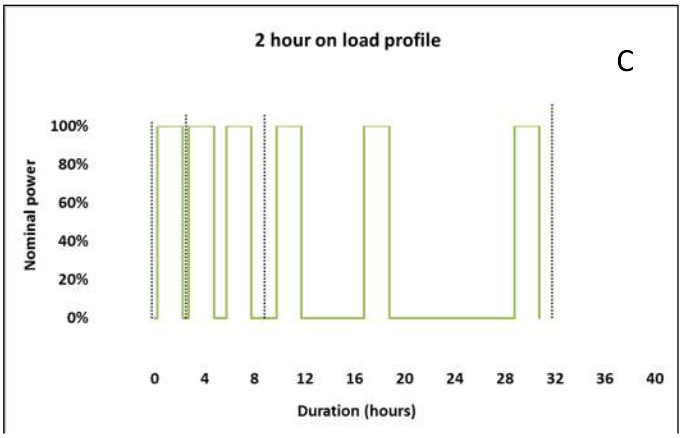
Specific studies carried out in HPEM2GAS for power to gas applications have identified relevant scenarios. According to this previous analysis, in some specific power-to-gas applications the run time of the electrolyzer can be as low as 30% temporal utilization, mainly at full load. In other words, the electrolyzer is operated only slightly in partial load operation. This occurs when there are high surplus capacities; in such case, it is to be expected that the electrolyzer will run under full load during periods of excess current, otherwise it will be shut down. This result is applicable in the case the only application envisaged for the electrolyser is exclusively related to power-to-gas. For the grid operator it is important to know the behaviour of the electrolyzer during the switching on and off processes. Specific protocols are thus useful at the stack/system level to address these aspects. However, before assessing the stack for operation under these conditions, it is useful to test the MEA with regard to such a scenario. The protocols are exemplified in the following:

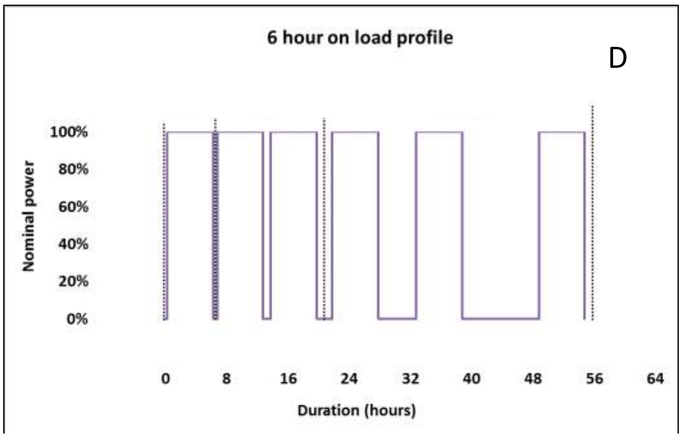
- Test A≡ Uptime: 15 min, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3A)
- Test B≡ Uptime: 1 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3B)
- Test C≡ Uptime: 2 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3C)
- Test D≡ Uptime: 6 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3D)

Uptime load profiles have been assessed in HPEM2GAS D2.2. These are reported below for convenience.









The specific protocol for the MEA is designed as follows:

Assessment of MEA dynamic behaviour: On-off cycles

Single cell durability study	MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks
Test Method: Single cell assessment	• Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of 4 ml/min/cm2 (ρ> 5 MOhm cm) • Set thermostat to desired temperature • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours at ambient pressure • Fix cut-off voltage to 2 V, for the selected current density range (up to 4 A cm^{-2}) • Carry out the BoT polarisation curve, ac-impedance spectroscopy as defined above; monitor H_2 concentration in O_2 • Followed by the step cycle reported in TEST A or TEST B or TEST C or TEST D: - Repeat this test until a total of 250 h operation is reached

	• Carry out EoT polarisation, ac-impedance spectroscopy and Cyclic voltammetry • 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 eventually 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

METRIC	**FREQUENCY**	**TARGET**
MEA Stability	250 h	Degradation <2% at 90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	250 h	<2 vol % H_2 in the O_2 at all loads. <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

2.4 ASSESSMENT OF PERFORMANCE, STABILITY AND DYNAMIC BEHAVIOUR OF THE STACK FOR OPERATION UNDER EXTREME CONDITIONS

Protocols for assessing the non-active components of the stack such as the bipolar plates have been already treated in a public deliverable of the HPEM2GAS project (D2.1 HPEM2GAS). The different operating conditions and applications of the NEPTUNE project do not affect such aspects. Thus, these protocols are not repeated here. Only protocols dealing with electrochemical assessment of performance, stability and dynamic behaviour of the stack for operation under extreme conditions in terms of temperature, pressure and current density are discussed here. Suggestions regarding stack failure analysis are also provided. These however can vary depending on the type of stack failure that has been registered.

At the time of preparation of this report there is no final document released by JRC about PEM electrolysis stack assessment. Thus, no comparison of protocols can be made at this time.

2.4.1 *Stack performance*

The components and configurations developed as part of this project are validated in terms of performance and stability in short stacks and full stack.

Stack testing is carried out under controlled conditions in designed test stations operating at specific temperatures and pressures with a specifically developed balance-of-plant.

Stack performance is assessed by polarisation curve at the beginning of the test. Voltage related to specific cells and overall stack voltages are monitored. The protocol is essentially similar to 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 in histograms. Results are thus interpreted in comparison to the single cell MEA assessment and according to the stack design.

Performance:

Assessment of stack performance

Stack polarisation curve	Stack assembling according to the project fabrication procedures and related checks
Test Method: Performance assessment	• Feed anode manifold with water at a rate of 4 ml/min/cm2 of total area (water resistivity: $\rho > 5$ MOhm cm) • Set water thermostat temperature at 30 °C • Fix cut-off voltage to 2.4 V/cell to cover the full range • Cell conditioning: apply a load of 0.2 A cm^{-2} for 24 hours to favour 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 H_2 concentration in oxygen at each current density • Decrease pressure at low current densities if needed (H_2 in O_2 >3%) • Repeat polarisation curve in ascending mode to check for hysteresis. • Carry out ac-impedance spectroscopy of specific cells and overall stack by modulating the load (e.g. using Gamry instrumentation). • Repeat tests at various temperatures (30 - 140 °C) and pressures (ambient - 10 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 specific current densities • Report ac-impedance spectra of the overall stack and specific individual cells. The reported cell temperature is the water temperature at the anode outlet.

METRIC	**FREQUENCY**	**TARGET**
Stack performance	BoT	>4 A·cm^{-2} at 1.75 V/cell at T>90 °C with PGM loading < 0.4 mg cm^{-2}; >6 A·cm^{-2} at E_{Cell} < 1.95 V at T>90 °C with PGM loading < 0.4 mg cm^{-2}; >8 A·cm^{-2} at E_{Cell} < 2.2 V at T>90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	BoT-EoT	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

2.4.2 *Stack stability*

Assessment of stack stability

Stack durability study	Stack assembling according to the project fabrication procedures and related checks
Test Method: Stability assessment	• Safety conditions as reported for the polarisation measurements. • Feed anode with water at a rate of 4 ml/min/cm2 of total area (water resistivity; ρ> 5 MOhm cm) • Fix 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 O_2 >3%) • Carry out BoT ac-impedance spectroscopy • Carry out a durability test of 2000 h at 4 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	2000 h test steady-state	Degradation <5 µV/h/cell in a 2000 h test, 4 A·cm^{-2}, with PGM loading < 0.4 mg cm^{-2};
Gas crossover	2000 h test steady-state	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

2.4.3 *Stack dynamic behaviour*

Overall dynamic behaviour of the stack (partial load, on-off) is assessed in combination with the balance of plant in the electrolysis system. This is discussed in the following chapter.
Here is discussed only the transient behaviour i.e. the stack capability to operate for a few hours at 6 and 8 A cm^{-2}

Assessment of stack dynamic behaviour: Transient operation Test 1

Stack transient operation	Stack assembling according to the project fabrication procedures and related checks
Test Method: Stack assessment of the dynamic behaviour	• Safety conditions as reported for the polarisation curve. • Feed anode with water at a rate of 4 ml/min/cm2 (water.: ρ> 5 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 • Fix 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 6-step cycle: - Step 1: 10 seconds at 0.2 A/cm^2 (5% load) - Step 2: 10 seconds at 4 A/cm^2 (100% load) - Step 3: 10 seconds at 6 A/cm^2 (150% load) - Step 4: 10 seconds at 8 A/cm^2 (200% load) - Step 5: 10 seconds at 6 A/cm^2 (150% load) - Step 6: 10 seconds at 4 A/cm^2 (100% load)

	- Repeat this test 1500 times to form a first set of accelerated stress test - AST (corresponding to ~25 h if all steps are included) • Carry out polarisation curve as defined above • Repeat AST to complete 5 sets of 1500 cycles (7500 cycles) correspond to 125 hrs dynamic operation with 5 diagnostic intervals • 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	7500 cycles	Degradation <5 µV/hr/cell, at 90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	7500 cycles	<0.2 vol % H_2 in the O_2 at 100 bars at 4 $A{\cdot}cm^{-2}$ if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

Assessment of stack dynamic behaviour: Transient operation Test 2

Stack transient operation	Stack assembling according to the project fabrication procedures and related checks
Test Method: Stack assessment of the dynamic behaviour	• Safety conditions as reported for the polarisation measurements. • Feed anode with water at a rate of 4 ml/min/cm2 of total area (water resistivity; ρ> 5 MOhm cm) • Set thermostat temperature at the desired value • Fix cut-off voltage to 2.4 V to cover the full range • Cell conditioning: apply a load of 1 A cm^{-2} for 100 hours at ambient pressure • Stabilize the selected cathode pressure (differential pressure) and water outlet temperature, at the anode compartment, at the maximum 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 O_2 >3%) • Carry out BoT ac-impedance spectroscopy • Carry out step cycle Test A or Test B; Test A: 3h at 4 $A{\cdot}cm^{-2}$ with 1 h interval at 6 $A{\cdot}cm^{-2}$; Test B: 3h at 4 $A{\cdot}cm^{-2}$ and 1 h interval at 8 $A{\cdot}cm^{-2}$

	• Repeat the chosen test until completing 10 cycles • Carry out EoT polarisation, ac-impedance spectroscopy • Report data as Stack Potential (V) vs. Time (h) along with temperature, pressure and catalysts loadings. Report cell 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	40 h AST	Degradation <5 µV/hr/cell, at 90 °C with PGM loading < 0.4 mg cm^{-2};
Gas crossover	40 h AST	<0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

2.4.4 Stack failure analysis

The first stack diagnostic is carried out in real time during operation by monitoring specific cells (e.g. terminal cells, middle position cells) and/or group 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 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

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 4 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 fixed at 1.5 V/cell in order to compare the data-set to that obtained in single cell MEA testing. However, for large area cells, if the current will exceed 20 A at this potential, the galvanostatic operating mode is selected with DC current of 10 A or higher and oscillation 1 A. The frequency range should be as close as possible to the one selected for single cell MEA testing (see above).

Cyclic voltammetry

Gas cross over and fluorides release

Protocols for *in-situ* crossover measurements of gases under practical operation include sensor methods and GC methods (H_2). Details of these operating procedures are reported in the MEA testing section.
Protocols for determining any fluoride ion release are based on the use of a fluoride sensitive electrode, pH meter. Water is analysed at both anode and cathode outlet.

Ex-situ physicochemical analysis

A post-operation physico-chemical analysis can be carried out on active (membrane, catalysts, MEAs) components to individuate any degradation effect related with practical 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.

2.5 ASSESSMENT OF SYSTEM PERFORMANCE, EFFICIENCY, STABILITY AND DYNAMIC BEHAVIOUR FOR OPERATION UNDER EXTREME CONDITIONS

The aim of the NEPTUNE project is to validate the advanced components and operation strategies in a practical electrolysis system. Although, there is no field-testing campaign in this project, it is important to assess the system for operation under different applications. These include grid-balancing service, power-to-gas, off-grid operation (direct interfacing to renewable power sources).
The electrolysis system is composed by the electrolysis stack and the balance-of-plant (BoP).
Although extreme operating conditions are primarily addressed by the properties of the membrane, catalysts, MEAs, also some components of the balance of plant have an important role and can help significantly in managing certain operating conditions.
In general, the BoP components must be designed to operate at the targeted hydrogen pressure and need to manage the heat release from the electrolyser during operation under exothermic mode (practical operation).
BoP components 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 behaviour for the PEM electrolysis system require that all these sub-systems are properly designed for operation under the targeted conditions.
In the system, the actual capacity is regulated by an electronic control system as well as by the pressure on the output tubes.
Special 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 that may derive from degradation of novel hardware components and the H_2-water separation. These cartridges should be capable of sustaining the increased operating temperature of the stack with the associated increase in the temperature of the recirculated water.

Another relevant system component is the power conditioning/control unit. This primarily addresses the effects the grid or renewable power fluctuations and together with the other sub-units should support the requested dynamic behaviour.

The protocols reported below first deal with an assessment of the system under stationary conditions for operation at high current density as well as at high pressure (up to 100 bar) and high temperature (up to 140 °C). Thus, some relevant targets of performance, efficiency, stability are assessed under stationary operation. Whereas specific protocols are designed to assess the dynamic behaviour. These essentially regard variable load and on-off operation.

At the time of preparation of this report there is no final document released by JRC about PEM electrolysis system assessment. Thus, no comparison of protocols can be made at this time.

2.5.1 System assessment under stationary conditions

Assessment of system performance under stationary conditions	
Validation of nominal hydrogen production capacity and system efficiency	System assessed with stack and BoP designed for operation at high current density, high temperature and high pressure
Test Method: Performance and efficiency assessment	• Set cut-off voltage at 2.4 V/cell • Operate the system at ~25% of nominal capacity and for sufficient time to guarantee appropriate stack/sub-system conditioning. • Operate the system at 100% constant load (4 A·cm^{-2}) at nominal temperature (up to 140 °C stack temperature), and pressure (up to 100 bar stack pressure) for 2000 hours (steady-state) • Shut-off the system • Determine the average hydrogen production rate • Report data as H_2 production rate and efficiency vs. time along with operating stack temperature and pressure.

METRIC	**FREQUENCY**	**TARGET**
System performance	BoT	Efficiency better than 80% HHV H_2 at 4 A cm^{-2}; Energy consumption lower than 50 kWh/kg H_2 at 4 A·cm^{-2};
System durability	BoT-EoT	Efficiency loss <2 %/year
Hydrogen quality	BoT-EoT	5N

2.5.2 System assessment under dynamic conditions

Assessment of system performance under dynamic conditions Test 1

Validation of dynamic behaviour	System assessed with stack and BoP designed for operation at high current density, high temperature and high pressure
Test Method: *Assessment of dynamic behaviour*	• Set cut-off voltage at 2.4 V/cell • Operate the system at ~100% of nominal capacity and for sufficient time to guarantee appropriate stack/sub-systems conditioning. • Followed by a 6-step cycle: - Step 1: 10 seconds at 0.2 A/cm^2 (5% load) - Step 2: 10 seconds at 4 A/cm^2 (100% load) - Step 3: 10 seconds at 6 A/cm^2 (150% load) - Step 4: 10 seconds at 8 A/cm^2 (200% load) - Step 5: 10 seconds at 6 A/cm^2 (150% load) - Step 6: 10 seconds at 4 A/cm^2 (100% load) - Repeat this test 1500 times to form a first set of accelerated stress test - AST (corresponding to ~25 h if all steps are included) - Repeat AST to complete 5 sets of 1500 cycles (7500 cycles) correspond to 125 hrs dynamic operation • Determine performance and efficiency decrease at the nominal current density. • Report transient response time and H_2 production rate and efficiency vs. time along with system load range, temperature and pressure.

METRIC	**FREQUENCY**	**TARGET**
Dynamic behaviour	BoT	Transient response achieved in 1 s.
System durability	BoT-EoT	Efficiency loss <2%/year
Load range	BoT-EoT	Load range 5%-200% corresponding to 0.2 A·cm^{-2} and 8 A·cm^{-2}
Gas crossover	BoT-EoT	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

Assessment of system performance under dynamic conditions Test 2

Validation of dynamic behaviour	System assessed with stack and BoP designed for operation at high current density, high temperature and high pressure
Test Method: *Assessment of dynamic behaviour*	• Set cut-off voltage at 2.4 V/cell • Operate the system at ~100% of nominal capacity and for sufficient time to guarantee appropriate stack/sub-systems conditioning.

	• Carry out step cycle Test A or Test B; Test A: 3 h at 4 A·cm^{-2} with 1 h interval at 6 A·cm^{-2}; Test B: 3 h at 4 A·cm^{-2} and 1 h interval at 8 A·cm^{-2} • Repeat the chosen test until completing 10 cycles • Report transient response time and H$_2$ production rate and efficiency vs. time along with system load range, temperature and pressure.

METRIC	**FREQUENCY**	**TARGET**
Dynamic behaviour	BoT	Transient response achieved in 1 s.
System durability	BoT-EoT	Efficiency loss <2%/year
Gas crossover	BoT-EoT	<2 vol % H$_2$ in the O$_2$ at all loads; <0.2 vol % H$_2$ in the O$_2$ at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

Assessment of system performance under conditions simulating power to gas applications

Power to gas applications	System assessed with stack and BoP designed for operation at high current density, high temperature and high pressure
Test Method: Assessment of dynamic behaviour under power to gas applications	• Set cut-off voltage at 2.4 V/cell • Operate the system at ~100% of nominal capacity, temperature and pressure for 24 hrs to guarantee appropriate stack/sub-systems conditioning. • Proceed with Test A for 430 hrs ≡ Uptime: 15 min, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3A) • Operate the system at nominal capacity for 24 hrs • Proceed with Test B for 430 hrs ≡ Uptime: 1 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3B) • Operate the system at nominal capacity for 24 hrs • Proceed with Test C for 430 hrs ≡ Uptime: 2 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3C) • Operate the system at nominal capacity for 24 hrs • Proceed with Test D for 430 hrs ≡ Uptime: 6 h, then downtimes: 15 min, 30 min, 60 min, 2 h, 5 h, 10 h (Fig 3D) • Operate the system at nominal capacity for 24 hrs • Determine performance and efficiency decrease at the nominal current density. • Report data as H$_2$ production rate and efficiency vs. time along with operating stack profile, temperature and pressure.

METRIC	**FREQUENCY**	**TARGET**
System performance	BoT	Efficiency better than 80% HHV H_2 at 4 A cm^{-2}; Energy consumption lower than 50 kWh/kg H_2 at 4 A·cm^{-2};
Dynamic behaviour	BoT	Warm Start-Up achieved in 1 s Cold Start-Up achieved in 10 s
System durability	BoT-EoT	Efficiency loss <2 %/year
Gas crossover	BoT-EoT	<2 vol % H_2 in the O_2 at all loads; <0.2 vol % H_2 in the O_2 at 100 bar at 4 A·cm^{-2} if a recombination catalyst is used. Quote temperature, pressure and current density, alongside values

3. TERMINOLOGY, EFFICIENCY AND DURABILITY

As discussed above, one of the aims of this activity is to align the internal procedures of the NEPTUNE project to the protocols and definitions reported by JRC in their harmonised documents on PEM electrolysis. JRC has already released a document on “EU HARMONISED TERMINOLOGY FOR LOW TEMPERATURE WATER ELECTROLYSIS FOR ENERGY STORAGE APPLICATIONS” and it is the aim of the NEPTUNE consortium to adopt this a base document for terminology.

CNR has collaborated with JRC on the harmonisation of the terminology for low temperature electrolysis including the definitions of efficiency for cell, stack and systems. It is important to point out that due to contribution of different stakeholders the resulting definitions are influenced by a number of compromises between the different requirements of the various programs which are carried out. Thus, in some cases, there is more than one definition for a single key performance indicator in the harmonised document. This is for example the case of the efficiency definition at single cell level. To provide a fair comparison of the results and achievements in this project with those obtained in other projects the set of equations, from the EU HARMONISED TERMINOLOGY document, specifically used here to determine efficiency at different levels and other key performance indicators are indicated. Full details about the different definitions, the cases where these are applicable, and the thermodynamic justifications are reported in the document EU HARMONISED TERMINOLOGY FOR LOW TEMPERATURE WATER ELECTROLYSIS FOR ENERGY STORAGE APPLICATIONS.

3.1 TERMINOLOGY AND EFFICIENCY DEFINITION

3.1.1 Energy efficiency

Energy efficiency is defined as the ratio between the total chemical energy output and the total energy input (electricity and heat).

Under standard reversible conditions (Standard Ambient Temperature and Pressure-SATP; 20 °C, 1bar abs), the electrolysis process can occur when an amount of energy equal to ΔH^0 is supplied:

$\Delta H^0 = \Delta G^0 + T\Delta S^0$

Where ΔH^0 is the standard reaction entalpy, ΔG^0 is the standard free energy change, and ΔS^0 is the standard reaction entropy.

ΔH^0 = 285.84 kJ mol^{-1} H_2 (enthalpy or energy required to split water under reversible conditions)
ΔG^0 = 237.22 kJ mol$^{-1}H_2$ (reversible electrical work)
$T\Delta S^0 = Q_{rev}$=48.6 kJ mol^{-1} (reversible heat)

At the thermo-neutral potential, U_{tn}, there is a heat balance between the thermal energy transferred to the cell and that produced by the cell. This is linked to the reaction enthalpy and the higher heating value (HHV) from the equation:

$U_{tn}^0 = \Delta H^0 / (n\ F)$ where ΔH^0 = HHV = 285.84 kJ mol^{-1} H_2 (U_{tn} = 1.4813 V) at SATP conditions.

Under irreversible conditions, one must consider the effective energy supplied to the cell to produce water electrolysis both in terms of heat and electricity:

Supplied electrical work = $n \cdot F\ U_{cell}$
Supplied heat = Q_{input}

Under practical conditions, the amount of supplied electricity is usually significantly higher than the thermodynamic requirements in order to speed up the reaction rate. This is accompanied by a lot of internal energy dissipation as heat.

The reaction is endothermic when $U_{rev} < U_{cell} < U_{tn}$, whereas when the operating cell voltage $U_{cell} > U_{tn}$, the reaction is exothermic.

During exothermic operation, the heat required by the reaction ($T\Delta S$) is provided in-situ by the internal dissipation (activation, mass transfer overpotentials and ohmic dissipations).

Being the energy efficiency defined as the ratio between the total chemical energy output and the total energy input (electricity and heat), the energy related efficiency can be defined as follows:

$$\varepsilon_{cell} = \frac{\Delta H_{rev}}{nFU_{cell} + Q_{input}} = \frac{n \cdot F \cdot U_{tn}}{nFU_{cell} + Q_{input}} \qquad \text{(cell efficiency general case)}$$

In this equation, it is assumed that there are no hydrogen losses due to the crossover.

If the external heat is supplied by heating the water at the inlet, e.g. to bring the temperature of the water at the desired operating temperature, Q_{input} can be determined as follows:

$Q_{input=}$thermal power·time=$P_{thermal}$ (J/s)·t (s)

$P_{thermal}$= water flow · water thermal capacity·ΔT

$$P_{thermal} = \dot{m}_{H_2O} \cdot \mathrm{Cp} \cdot \Delta\mathrm{t}$$

$\dot{m}_{H_2O}$ is provided in (g/s)

Water heat capacity under standard conditions Cp= 4,18 J/(g·K)
ΔT= $T_{out,\ cell}$ –$T_{in,cell}$ (K)

This approach can give information on the effective heat exchange between the cell and the surroundings. If $\Delta T<0$ the reaction inside the cell is endothermic and the effective heat provided to the cell to heat the water at the desired temperature must be considered in the efficiency equation.

If the cell operates above the thermoneutral potential, the heat internally produced in the exothermic irreversible process is larger than the required reversible heat associated to the entropy variation of the process and thus no external heat is needed by the cell (cooling is possibly needed). In this case, since the heat supply is essentially zero (Q_{input}=0)

$$\varepsilon_{cell} = \frac{n{\cdot}F{\cdot}U_{tn}}{n{\cdot}F{\cdot}U_{cell}} = \frac{U_{tn}}{U_{cell}} < \ 1 \qquad \text{(cell efficiency exothermic case)}$$

Also, in this case it is assumed that there are no hydrogen losses due to the crossover.

$\frac{U_{tn}}{U_{cell}}$ can be also reported as the voltage efficiency.

Since the nominal operating current density targeted in the project is 4 A cm^{-2} that in a practical system corresponds to an operating condition well above the thermoneutral potential, the exothermic case is the one usually occurring in NEPTUNE.

However, for partial load operation of a cell or stack in combination with external heat supply, the general case efficiency equation must be used.

If the cell or the stack operate above the thermoneutral potential and there is no external heat supply, i.e. all energy requirement is provided as electrical energy, the efficiency decreases progressively with the increase of the supplied electricity from the thermoneutral potential.
No reaction should occur below the thermoneutral potential when there is no external heat supply being the electrical energy not sufficient to cover the ΔH. Instead if there is an external heat supply this can in part or in total cover the reversible heat requirement TΔS. Thus, in principle, when the supplied heat is equal or larger than Q_{rev} the reaction could occur starting from the reversible potential (1.225 V at SATP conditions) associated to the free energy change.

In this case, efficiency is a function of two variables i.e. electricity supply (nF U_{cell}) and external heat supply (Q_{input}) as represented below.

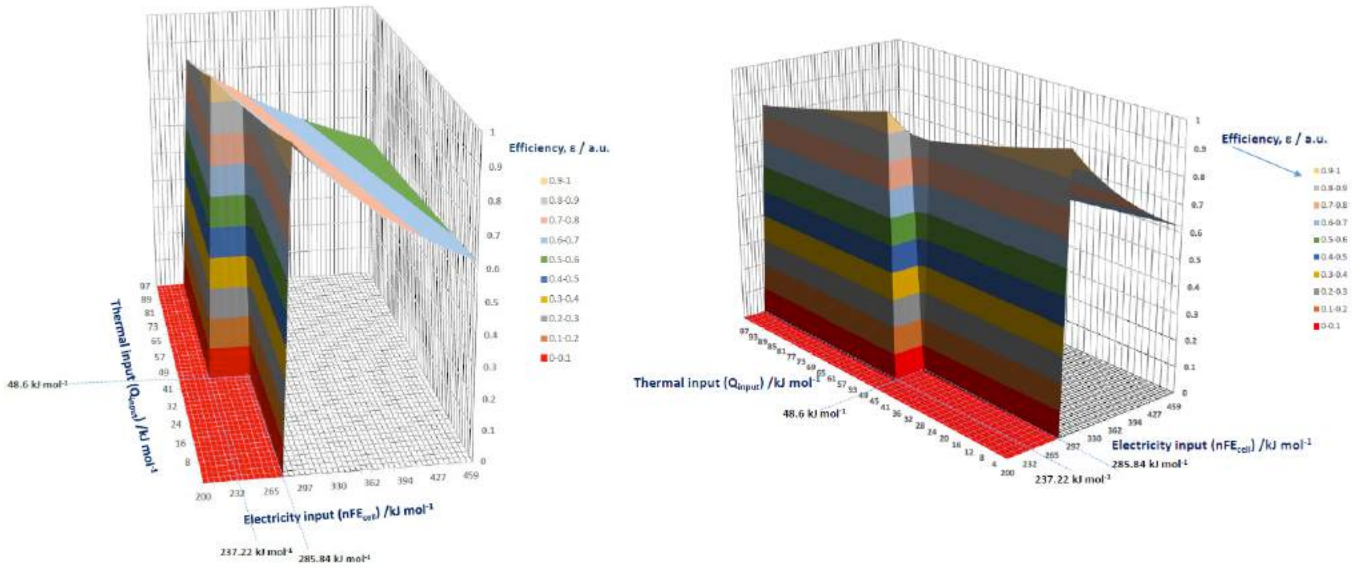


Fig. 4 Variation of the energy efficiency for water splitting as function of electricity and heat supplied.

3.1.2 Faradaic efficiency

Since some hydrogen is lost due to permeation through the membrane or in a recombination process with oxygen due to the gas crossover, the faradaic efficiency must be also considered.

The cell faradaic efficiency at the 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 second multiplied by the Faraday constant and the provided direct current, I_{DC} expressed in Ampere.

$$\eta_{I\ stack}^{H_2} = \frac{measured\ H_2\ flow\ rate}{theoretical\ H_2\ flow\ rate} = \frac{2 \cdot F \cdot \dot{n}_{H_2\ measured}}{I_{DC}}$$ (cell faradaic efficiency)

3.1.3 Overall cell efficiency

The total efficiency η_ω is defined as the product of energy efficiency and faradaic efficiency values.

$$\eta_\omega^{cell} = \varepsilon_{cell} \cdot \eta_I^{cell}$$ (cell overall efficiency)

3.1.4 Stack efficiency

The same considerations apply to the case of a stack characterised by N cells:

$$\varepsilon_{stack} = \frac{N \cdot n \cdot F \cdot U_{tn}}{N \cdot n \cdot F \cdot U_{cell} + Q_{input}}$$ (stack energy efficiency general case)

$$\varepsilon_{stack} = \frac{N \cdot U_{tn}}{U_{stack}}$$ (stack energy efficiency exothermic case)

$$\eta_{I\ stack}^{H_2} = \frac{measured\ H_2\ flow\ rate}{theoretical\ H_2\ flow\ rate} = \frac{2 \cdot F \cdot \dot{n}_{H_2\ measured}}{N\ I_{DC}}$$ (stack faradaic efficiency)

Total stack efficiency is thus the product of the energy (or voltage efficiency) by the faradaic efficiency.

$\eta_{\omega}^{stack} = \varepsilon_{stack} \cdot \eta_{I}^{stack}$ (overall stack efficiency)

Alternatively, the efficiency of both cell and stack can also be determined by measuring the effective hydrogen production rate and the total power input.

$\boldsymbol{\eta}^{\boldsymbol{HHV}} = \frac{\boldsymbol{HHV}}{\boldsymbol{P_{thermal}} + \boldsymbol{P_{electrical}}} \cdot \dot{\boldsymbol{n}}_{\boldsymbol{H_2}}$ (overall stack efficiency)

3.1.5 System efficiency

In a practical system, the overall energy consumption is deriving from the stack consumption and the consumption from the auxiliaries.
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 second multiplied by the HHV expressed in J·mol^{-1}, and the total thermal and electric power supplied to the system, for the operation of all ancillary equipment, expressed in Watt. It is expressed in percentage as:

$\eta_{system}^{HHV} = \frac{HHV}{P_{system\ extern}} \cdot \dot{n}_{H_2}$ (overall system efficiency)

Usually for practical PEM electrolysis systems, the total energy supplied is essentially electric energy.

The efficiency of a PEM electrolysis system can be also determined by comparing the theoretical energy consumption (HHV 39.4 kWh/kg H_2) to the effective system overall energy consumption per kg of produced H_2.

3.1.6 Durability

The absolute value of rate of decay of performance is generally reported in terms of voltage increase per hour, at constant current density (µV/h). This can be determined using the best fit of the curve of cell or stack voltage versus time.
Usually, the first 100 hrs are excluded from this analysis since during the first phase of cell/ stack conditioning the voltage variation with time is quite different. In the first conditioning phase, the voltage change with time could be also negative since different phenomena may occur in situ that improve cell performance. In other systems, this is the case of metallic Ir anode catalyst, the negative variation of voltage with time can persist for thousands of hours but the initial cell voltage is relatively higher (lower efficiency) compared to Ir-oxides. This reflects the transformation from metallic Ir into Ir oxide.

Thus, in general, it would be helpful to reference the recorded degradation rate to the initial cell voltage. In fact, a significant voltage increase with time may not be dramatic if the initial cell voltage is sufficiently low (high efficiency operation) making the potential window for practical operation wider.
A useful parameter to assess the stability characteristics can be defined as the reciprocal of the product between the voltage increase rate and the initial cell overvoltage versus the thermoneutral potential (~ 1.48 V at 25°C).

$$\text{Stability Factor (SF)} = \frac{1}{\text{Voltage increase rate} \cdot \text{Initial cell overvoltage}} = h \cdot V^{-2}$$

4. TABLES OF CHARACTERISATION DATA

It is useful to collect project results in a table dealing with characterisation data. This to harmonise how data reporting is addressed in the project and favour homogeneity of treated important indicators.

Membrane:

	unit	**result**	**method**
Polymer type			
Batch No			
Reinforcement			
Appearance (colour)			
IEC (ion exchange capacity)	meq g^{-1}		
EW (equivalent weight)	g eq^{-1}		
Thickness (dry)	µm		
Water uptake Δm in H_2O at specific T °C	wt %		
Thickness increase Δz in H_2O at specific T °C	%		
MD increase Δx in H_2O at specific T °C	%		
TD increase Δy in H_2O at specific T °C	%		
Through plane conductivity in H_2O at specific T °C	mS cm^{-1}		
Area resistance in H_2O at specific T °C	Ω cm^2		
In plane conductivity in H_2O at specific T °C	mS cm^{-1}		
H_2 permeation	cm s^{-1}		
O_2 permeation	cm s^{-1}		
Young's modulus at specific T °C	MPa		
Tensile strength at specific T °C	MPa		
Elongation break at specific T °C			
Start of thermal decomposition	°C		
Glass transition temperature T_g	°C		
Differential pressure resistance			
Oxidative stability (mass loss)	%		
Hydrolytic Stability			
Other mechanical properties			

Electrocatalysts or electrocatalyst-electrolyte interface:

	unit	result	method
Catalyst formulation			
Batch No			
Application as anode or cathode			
Bulk and surface composition			
Physico-chemical parameters: structure			
Physico-chemical parameters: particle size/crystallite size	nm		
Electrochemically active surface area	m^2/g; mC/mg along with sweep rate mV s^{-1} mC cm^{-2} mC/mg along with sweep rate mV s^{-1}		
OER overpotential (IR-free) at 4 A cm^{-2} at specific loading (mg cm^{-2}) in the presence of specific membrane, temperature (°C) and pressure (bar) conditions	mV		
Cathode overpotential vs. RHE at 4 A cm^{-2} at specific loading (mg cm^{-2}) in the presence of specific membrane, temperature (°C) and pressure (bar) conditions	mV		
Stability: Electrochemical surface area loss in durability and accelerated tests vs. initial conditions	%		

MEA:

	unit	result	method
MEA formulation (anode, cathode, membrane, diffusion layers)			
Batch No			
Overall PGM loading in the MEA; specific cathode and anode loadings	mg; mg/cm^2		
Performance (cell voltage) at 4 A cm^{-2} and 8 A cm^{-2} at specific temperature (°C) and pressure (bar) conditions	V		
Performance degradation (cell increase) in steady-state tests at 4 A cm^{-2} at specific temperature (°C) and pressure (bar) conditions. Indicate operating turnover frequency	µV/h/cell		

Performance degradation in accelerated tests at specific temperature (°C) and pressure (bar) conditions	% loss		
H_2 Crossover effects	% of H_2 in O_2		
Total area specific resistance at specific current density or voltage, at specific temperature (°C) and pressure (bar) conditions – Low frequency resistance	Ohm cm^2		
Series resistance at specific current density or voltage, at specific temperature (°C) and pressure (bar) conditions – High frequency resistance	Ohm cm^2		
Polarization resistance at specific current density or voltage, at specific temperature (°C) and pressure (bar) conditions – Difference between low and high frequency resistance	Ohm cm^2		

Stack:

	unit	**result**	**method**
Stack characteristics (N° cells, geometrical area etc.)			
Code No			
Overall PGM loading per cell and in the stack; specific cathode and anode loadings per geometrical electrode area	mg; mg/cm^2		
Performance (stack voltage, and normalised per cell) at 4 A cm^{-2} and 8 A cm^{-2} at specific temperature (°C) and pressure (bar) conditions	V V/cell		
Performance degradation (stack voltage increases normalised per cell) in steady-state tests at 4 A cm^{-2}, at specific temperature (°C) and pressure (bar) conditions	µV/h/cell		
Performance degradation in accelerated tests at specific temperature (°C) and pressure (bar) conditions	% loss		
H_2 Crossover	% of H_2 in O_2		
Energy consumption (polarisation curve)	kWh/kg H_2 at nominal production rate		
Efficiency	% vs. HHV of H_2 at 4 A cm^{-2} current density		
Voltage decay in dynamic tests	µV/h/cell		

System:

	unit	**result**	**method**
System characteristics (stack type, BoP specifications, control unit etc.)			
Code No			
Overall PGM loading in the system; specific cathode and anode loadings per geometrical electrode area	mg; mg/cm^2		
Nominal capacity: at specific temperature (°C) and pressure (bar) conditions	kg H_2/day		
Energy consumption (polarisation curve)	kWh/kg H_2 at nominal production rate		
Efficiency	% vs. HHV of H_2 at nominal capacity		
Hydrogen quality	% (N)		
Operational capacity range	% load range		
Cold start up (from off to nominal capacity)	min		
Load ramp up (from 5% to 100%)	s		
Performance loss in duty cycles	% decrease hydrogen production rate /year		
Total hydrogen production in field tests	tons H_2		

5. ASPECTS RELATED TO SAFETY ISSUES

Safety is an important aspect of the research activity on electrolysis. The project will provide information to JRC on the safety aspects for the advanced high temperature, high pressure electrolysis technology in order to allow them to extend the set of operating conditions in their analysis. Any safety-related event that may occur during the execution of the project will be reported to the European Commission's Joint Research Centre (JRC), which manages the European hydrogen safety reference database, HIAD.

Hydrogen is a highly flammable gas. Ensuring the electrolytic generation of hydrogen is performed safely is critical to the successful implementation of electrochemical hydrogen production. A short overview of the most important safety aspects addressed in NEPTUNE is provided below. This is in no way all-encompassing but is rather intended as an introduction. Further information should be sought from international references [http://h2bestpractices.org/, and http://www.hydrogensafety.info/]

Being such a small molecule, hydrogen is prone to leaking. Combining with its low-energy ignition, wide range of combustible fuel-air mixtures and its ability to cause embrittlement of metals means extra caution needs to be taken and the environment monitored at all times. Plastic or elastomeric materials used within classified areas must not be allowed to build up static charge. All classified areas should have both low and high oxygen sensors and hydrogen sensors.

All materials used in the construction of an electrolyser must be suitable for the range of temperatures and pressures to which the electrolyser is subjected to.

The system to be developed will include remote monitoring/control and safety functions in relation to the operation up to 100 bar and at a temperature up to 140 °C.

High pressure operation necessarily would require the use of thick membranes to maintain the critical concentrations (mostly H_2 in O_2) under the safety threshold (<25% LEL) but the high performance and efficiency targets will need to focus on thin membrane. Thus, there is the need to manage the gas crossover by appropriate means to avoid reaching the flammability limit especially at the anode compartment under differential pressure operation.

In addition to this, the reaction between hydrogen and/or oxygen with all materials used in the construction of the electrolyser must be very slow. In general, the materials used must resist degradation due to the chemical and physical action of fluids within the electrolyser. When selecting materials due consideration must also be given to wear resistance, and galvanic corrosion.

The nature of electrolyser development is such that sampling of liquids or gases is often necessary. Precautions need to be taken in the design of the take-off points, and these points should be marked appropriately.

Pressure relief valves must be used on pressurized systems to prevent over-pressurization. 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 explosive limit of hydrogen in oxygen or air is 4% (by volume). However, gas mixtures must remain below 1-2% volume fraction of hydrogen in oxygen within the hydrogen generator to avoid risks. Both passive and active means can be used to ensure this protective level is adhered to.

The polymeric electrolyte used within PEM electrolysers must be chemically stable over the operating conditions of the electrolyser. It must not release any chemicals nor catalyse any parasitic reactions that can contaminate the product gases of hydrogen or oxygen. Membrane failure can result in an explosive mixture of gases; therefore, all electrolyser devices need to incorporate monitoring devices to monitor the effects of membrane instability.

The oxygen evolution reaction has its own demands on the system. When pressurised oxygen is used, some materials can 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 the material will see.
Hydrogen electrolysis has the potential to make a large positive impact on the environment. Unsafe practices can set this back, often years. Education of hydrogen safety is critical to making hydrogen a consumer used fuel that is used safely and responsibly.

6. CONCLUSIONS

This deliverable is dealing with protocols and procedures to assess the achievements of the project targets, with regard to hydrogen generation in a wide range of operating temperature, pressure and current densities. In addition, the protocols dealing with electrolyser assessment for operation under dynamic conditions are also defined. These will be refined during the execution of the project.

An important aspect has regarded the implementation in the NEPTUNE project of the harmonised characterisation protocols developed by the Joint Research Laboratory of the European Commission (JRC-IET) for testing MEAs & stacks. These protocols have been extended to cover extreme operating conditions addressed in NEPTUNE.

In general, the protocols here defined will enable planning of the test activities in WP3, WP4, WP5 and WP6.

The procedures discussed in this deliverable report include validation of active components, MEAs, stack and PEM electrolysis systems. Thus, these procedures will provide a systematic approach to assess materials, components, and systems for hydrogen generation under specific operating conditions.
The aim is also to compare system performance with stack and single cell performance at specific current densities and to determine energy consumption under different conditions of temperature and pressure. A relevant aspect regards the durability of the PEM electrolysis system under these extreme conditions. For this purpose, assessing performance degradation under steady-state tests and duty cycle operation play an important role.
These protocols are primarily addressed to assess the specific NEPTUNE project objectives and milestones; however, the aim is also to contribute to the harmonization efforts of JRC for testing PEM electrolysis components and devices in order to contribute to establishing agreed and shared procedures among the community of electrolysis stakeholders.