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**High Performance PEM Electrolyser for Cost-effective Grid
Balancing Applications**



HPeM2GAS - Deliverable report

**D2.1 Protocols for characterisation of system components
and electrolysis system assessment**

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Summary

The deliverable 2.1 “Protocols for characterisation of system components and electrolysis system assessment” regards detailed characterisation procedures for testing both relevant electrolysis components and balance-of-plant (BoP). The procedures addressed in this deliverable are defined to assess the electrolysis system both in stationary conditions and with reference to its capability to work in grid balancing service. The latter aspect deals with the dynamic behaviour of the electrolysis system and its capability to support the local electrical grid at the Emden city council, Germany. This grid shares a large amount of installed wind and solar power plants.

The specific contents of the deliverable D2.1 are:

- Definition of a set of protocols for assessing PEM water electrolysis (PEMWE) components i.e. mapping of system level requirements to component level requirements.
- Definition of a set of protocols for assessing the PEM electrolysis system under stationary conditions in terms of performance, efficiency & durability including accelerated stress tests (AST).
- Definition of a set of protocols for the assessment of PEM electrolysis system under specific duty cycles related to grid-service application and in field tests.

The protocols defined in D2.1 are aiming to enable a proper planning of the test activities especially those in WP3 to WP6. In particular, the protocols describe a set of characterisations of system components (BoP, control unit, full stacks, large area membranes, scaled-up catalysts and MEAs) and establish a data-set of characteristics for which progress is assessed in terms of durability, efficiency and performance.

Specific efforts were addressed to include in this deliverable procedures from EU harmonised test protocols according to specific initiatives carried out in the framework of the FCH JU program.

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1 Introduction

This document deals with characterisation and test protocols for the assessment of performance, efficiency, durability and dynamic behaviour of electrolyser systems. The aim is also to implement protocols from previous FCH JU projects, to propose updated procedures and harmonize these procedures with other currently running initiatives in the framework of the FCH JU program, involving the European Commission and other stakeholders.

In this regard, some HPEM2GAS partners (CNR, ITM) have actively participated to the initiative of the JOINT RESEARCH CENTRE-EUROPEAN COMMISSION (JRC-IET) aiming at defining a set of protocols and testing procedures valid for assessing electrolysis devices with respect to the Key Performance Indicators (KPIs) defined in the Multi-Annual-Work Plan of the FCH JU (EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS).

IRD has actively contributed in defining/reviewing protocols for electrolysis within an initiative of the International Energy Agency (IEA).

Moreover, procedures from previous FCH JU projects, such as Electrohypem (G.A. 300081), were acquired and implemented with respect to the new requirements of HPEM2GAS, specifically in terms of updated KPIs. The aim was to form, together with the contribution obtained from other currently running initiatives, a set of protocols for assessing the PEM electrolysis devices developed in HPEM2GAS against the milestones, objectives and quantitative targets defined in the project.

A harmonised set of test protocols, when produced by a group formed by a significant number of stakeholders, may result in a number of compromises between the different requirements of the various programs which are carried out. It is clear that such general 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.

Accordingly, based on the specific requirements of the HPEM2GAS project, it was preferred to delineate for some KPIs, two sets of protocols. One is for specific use internal to the HPEM2GAS project and another parallel set of protocols is derived from the document on harmonised electrolysis procedures produced by JRC (EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS). This was prepared with the active contribution of several FCH JU program actors including the HPEM2GAS partners and other important international stakeholders. The JRC document is intended for general use whereas the internal protocol is aiming to assess the achievement of project milestones as indicated in the Description of Work.

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. Moreover, since the set of protocols from JRC should be hopefully adopted, widely, within the FCH JU program (FCH JU projects), this will provide a useful basis for comparison. This approach is in accordance with the aim of harmonising testing procedure expressed in the contents of Workpackage 2.

It is important to note that the set of protocols from the harmonised JRC document are essentially dealing with single cell/short stack testing whereas those from previous FCH projects were especially covering protocols from cell components to short stack testing. This deliverable is instead providing a complete set of protocols that

includes full stack and system characterisation in stationary conditions, duty cycle conditions, representative of grid-balancing service and for specific field-testing.

This is the first deliverable for the Work Package 2 – Specification, Harmonisation and regulation for grid services. WP2 is addressing 3 different tasks:

- Task 2.1 Harmonisation of characterisation and test protocols for the electrolysis system
- Task 2.2 Procedures for field testing
- Task 2.3 Energy policies and regulations for electrolysers application in grid-balancing service

The deliverable 2.1 is essentially regarding Task 2.1 but also includes aspects relevant to task 2.2. It is related to the detailed characterisation procedures for testing and includes both relevant electrolysis components & BoP specifications.

These procedures are not just aiming to assess the electrolysis system in stationary conditions but also with reference to its capability to work in grid balancing service.

The specific contents of the deliverable 2.1 are:

- Definition of a set of protocols for assessing PEM electrolysis components i.e. mapping of system level requirements to component level requirements.
- Definition of a set of protocols for assessing the PEM electrolysis system under stationary conditions in terms of performance, efficiency & durability (including accelerated stress tests or AST).
- Definition of a set of protocols for the assessment of the PEM electrolyser system in relation to the operation under specific duty cycles related to grid-service applications and in field tests.

These protocols describe a set of characterisations of system components (BoP, control unit, full stacks, large area membranes, scaled-up catalysts and MEAs) and establish a data-set of characteristics for which progress is assessed in terms of durability, efficiency and performance.

2 Definition of a set of protocols for assessing PEM electrolysis components

The membrane-electrode assembly (MEA) is the core of a PEM water electrolyser. This is built up around the proton exchange membrane (Aquivion® in the present project) that is in direct contact with two electro-catalytic layers, which generate hydrogen and oxygen. These are facing the gas-diffusion layers which allow gases escaping from the cell and facilitate water distribution on the electrode area.

The role of the MEA and its components is fundamental in determining performance, stability and cost of the PEM electrolysis system as well as its capability in addressing operation in grid-balancing service.

2.1 Membrane assessment

HPEM2GAS elaborates on previous research projects on PEM water electrolysis (e.g. ELECTROHYPEM) where a candidate perfluorosulfonic membrane for water electrolysis i.e. Aquivion® was developed and tested in small electrolysis systems. The objectives of the HPEM2GAS project are to produce a further scale-up of the Aquivion® membrane and to carry out an implementation of this membrane for application in grid-balancing service. This requires to assess membrane properties in terms of conductivity, high temperature operation, gas crossover, mechanical and electrochemical stability. In particular, during operation in grid-balancing service, it will be necessary to operate the system, for short time periods, at a load as much as 150-160% of the nominal load (peak shaving, load shifting), to carry rapid warm and cold start procedures etc. Under such conditions, a high membrane conductivity, in a wide temperature range, and the capability to sustain high heat release, corresponding to an increase of current density/operating temperature, even if for short periods, play a relevant role. Moreover, the objectives of the HPEM2GAS project deal with an operating pressure up to 80 bars which extends the operating conditions of the previous projects. This requires that the membrane must be mechanical stable under high differential pressure conditions.

The main targeted improvements indicated in HPEM2GAS for the properties of the proton exchange polymer electrolyte membrane are:

- Increase the membrane area for short side chain stabilised PFSA Solvay Aquivion® membranes up to 415 cm²;
- Reduction of membrane thickness to less than 90 µm for large area membranes in order to decrease ohmic resistance;
- Reduction of gas crossover for both H₂ and O₂ in large-area membranes in a wide range of current densities (from 0.5 to 3 A cm⁻²);
- Increase of proton conductivity and operating temperature up to 140°C under pressure;

A set of procedures is thus defined to select, on a large scale, the most promising polymer electrolytes among the refined/optimised Aquivion® membranes. This is essentially based on a wider range of characterisation protocols established in a previous FCH JU project Electrohypem to down select the most promising membranes from a large range of materials. However, in the present case, it is essentially comprising a minimum set of procedures to assess the implemented Aquivion® membrane for operation under critical conditions relevant to PEM electrolysis application in grid-balancing service.

Description of these methods is reported below. These methods are specific of perfluorosulfonic acid membranes such as Aquivion®, in particular the scaled-up and optimised membranes, and possibly not applicable to membranes of different chemistry. The aim is to produce a data-set table identifying membrane characteristics for such specific application (see Appendix A).

2.1.1 Membrane Properties

Determination of polymer chemistry and eventual reinforcement material.

Conventional chemical analysis; molecular weight etc.

Membrane pre-treatment before use:

- 1 M H₂SO₄ at T = 80 °C for 5 hours
- rinse in demineralised water;
- store in demineralised water

Ion exchange capacity: membrane equilibration in 0.1 M NaCl at RT for 12 hrs followed by titration with 0.1 M NaOH. IEC measured by titration as above. Data to be reported in meq/g (3 d.p.), 1 eq = 1 mol of SO₃H EW measured in g/eq.

Thickness: Membranes initially conditioned prior to testing

Thickness measured across the membrane using a micrometer screw gauge. **(MS1)**

Mechanical properties: stress-strain, speed 0.25 mm/min.

Ionic Conductivity: assessment in a wide range of temperatures (R.T. to 140 °C, in steps of 10 °C), pressure (ambient pressure, 3 bar, 5 bar with further steps of 5 bar). Methods: in-plane or through plane / 4-electrode set-up, AC impedance, high frequency intercept. **(MS1)**

Uptake of water: Equilibration for 1 h, removal of solvent from surface by tissue paper and measure the wet form followed by measuring the weight of dry sample after vacuum treatment at 80 °C.

% Water Uptake (WU) is defined by:

$$\% \text{ WU} = ((\text{hydrated mass} - \text{initial mass}) / \text{initial mass}) * 100$$

% Water Content (WC) is defined by:

$$\% \text{ WC} = ((\text{hydrated mass} - \text{dry mass}) / \text{hydrated mass}) * 100$$

Dimensional swelling: (three dimensions as function of time and temperature): immersion for 4 h in water at the relevant temperature in a closed glass or plastic bottle. Several 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 2d.p.

Samples then dried to constant mass in desiccator

% Linear Expansion Coefficient (LEC) is defined by:

$$\% \text{ LEC} = ((\text{hydrated length} - \text{initial length}) / \text{initial length}) * 100$$

Chemical and thermal stability (TGA-DSC): RT to 900 °C in air or nitrogen atmosphere at a heating rate of 2 °C/min.

Glass transition temperature (DMA): from RT to 400 °C in air at a heating rate of 2 °C/min, frequency 1 Hz, T_g at maximum of tan(δ).

Oxidative Stability: Fenton’s Reagent Test - 3% H₂O₂, 4 ppm Fe²⁺ ions at 60 °C for 4 h. Measure mass loss. This test will be applied only in the case a significant variation of membrane chemistry is required. Such test have already been carried out on Aquivion® in previous projects.

Chemical and Hydrolytic Stability: Release of fluorine species is measured as function of time during time-tests under electrolysis conditions.

2.1.2 In-situ membrane characterization

In-situ membrane characterization: This is dealing specifically with the membrane properties and includes *in-situ* conductivity measurements at various pressures, temperatures and operating current densities (i.e. under load this influences the electro-osmotic drag) using AC-impedance spectroscopy. The series resistance determined by the high frequency intercept on the real axis of the Nyquist plot will be used to determine the ohmic resistance. This will be subtracted by the resistance contribution of electrodes and hardware measured in a separate test. The conductivity will be thus determined by normalising the results by the membrane thickness and electrode area according to the general formula. This approach allows information about the conductivity under real operating conditions to be gathered. It will provide interface resistance assessment by comparing the values determined *in-situ* under OCV with those measured *ex-situ*.

Gas crossover: H₂ and O₂ permeability are measured by using specific sensors under electrolysis operation or in OCV under differential pressure or in a driven mode using the conventional electrochemical methods (**MS1**). Regarding the Differential Pressure Cell, this is a cell specifically designed at ITM that can be pressurized hydrostatically to 30 bar or pneumatically up to 100 bar. (**MS1**) The tests will assess burst pressure under various conditions and generally how the membrane and/or an MEA respond to pressure.

Gas crossover using the Driven-cell mode:

The hydrogen crossover rate through the membrane is assessed via an electrochemical method at relevant temperatures and pressures. The membrane is assembled in a standard test cell with hydrogen flowing on one side of the membrane and water on the other. A potentiostat is used to sweep the potential. The current resulting from the oxidation of molecular hydrogen is measured and used to calculate the hydrogen crossover rate.

Membrane Permeability to Hydrogen Gas

Protocol and Metrics

| | |
|-----------------------|--|
| Membrane Conditioning | Hydrate according to standard method Measure the thickness of the hydrated membrane prior to cell assembly and report with the result |
| Test Conditions | |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |
| Voltage range | 0.1 V to 0.4 V and thereafter keep potential constant at 0.4 V |
| Scan rate | 5 mV/s |

| | |
|-------------|--|
| Test Method | <ul style="list-style-type: none"> Assemble cell with potentiostat to control voltage and measure current. The anode acts as the reference and counter electrode and the cathode acts as the working electrode. Set the temperature and pressure as required Flow 100% humidified hydrogen on anode (equiv. of 1.5 stoich at 1A/cm²) and de-aerated water on cathode (1 g min⁻¹ cm⁻²) to keep membrane hydrated Sweep cathode potential from rest potential (0.1 V) to 0.4 V against anode at 5 mV/s and thereafter keep potential constant at 0.4 V Report crossover rate at 0.4 V from the recorded steady-state current |
|-------------|--|

| METRIC | FREQUENCY | TARGET |
|----------------------------|-----------|--|
| Hydrogen crossover current | | <0.5 mA/cm ² |
| Hydrogen crossover rate | | <0.035 ml/min/cm ² hydrogen |

Gas crossover using the sensor method:

The hydrogen crossover is measured under operating conditions by placing a sensor in-line in the oxygen gas flow in alternative to the electrochemical method treated above.

Hydrogen Crossover Test

Protocol and Metrics

| | |
|---------------------------|---|
| Assembly | MEA in standard electrolysis cell as discussed below with water flowing |
| Sensor | E.g. HY-OPTIMA in-line in gas flow on O ₂ side, calibrated |
| Membrane thickness | Measure hydrated thickness prior to cell assembly |
| Temperature | Set as required, must be recorded and reported |
| Pressure | From balanced pressure to 10 MPa delta P, 1 MPa increment |
| Current Density | 0.3 A/cm ² |

| METRIC | FREQUENCY | TARGET |
|---|--------------------------|--------|
| % H ₂ in O ₂ | Steady state measurement | <0.5 % |
| Quote thickness, temperature, current density, pressure alongside values | | |

2.2 Electro-catalysts assessment

The aim of HPEM2GAS project is to implement PEM electrolysis stack components developed in previous projects on a larger scale and optimise such components for grid management. Concerning the electro-catalysts, the objective is to further optimise catalytic systems developed in a previous project Electrohypem, in particular mixed oxide catalyst composed of Ir and Ru oxides (anode) and carbon supported Pt cathode, and produce such materials on a proper scale as required to demonstrate the electrolysis system in grid balancing service. As well known, these noble metal based electro-catalysts contribute to performance, stability and cost of PEM water electrolyzers since they are used at relevant loadings. The aim of the HPEM2GAS is to reduce the noble metal loading while keeping the performance and stability at proper levels. A good electro-catalytic activity is essential to achieve a low overpotential at high current densities (3 A cm^{-2}) as targeted in this project whereas an enhanced stability can increase significantly the life-time and reduce the number of stack replacements in a typical 20-year electrolyser life-span.

Accordingly, the aim is not to carry out a screening of catalyst properties since selected formulations have already been identified but to scale-up and optimise such formulation and to prove through a set of characterisation procedures that these catalysts characteristics are also valid for application on a large scale (180-300 kW) and in the presence of specific duty cycles deriving from fluctuation of the power supplied by the grid.

The main targeted improvements indicated in HPEM2GAS for the electro-catalysts are:

- Upscaling of the production of catalyst formulations, selected from previous projects, to large batches, i.e. larger than the nominal amount requested by the 180 kW PEM electrolyser stack;
- Optimising the electro-catalyst properties for large batch production in order to achieve high current densities at low overpotentials. In particular, the aim is to determine the anode overpotential vs. thermoneutral potential at specific current densities of practical interest for the project, e.g. 3 A cm^{-2} , from IR-free polarisation curves and the cathode overpotential vs. RHE at the same current densities defined for the anode. This in the presence of specific amounts of low noble metal loadings (e.g. anode Ir+Ru $< 0.4 \text{ mg cm}^{-2}$, cathode Pt $< 0.1 \text{ mg cm}^{-2}$).
- In particular, what is important for the specific HPEM2GAS project is that the selected combination of anode and cathode catalyst can cumulatively operate to achieve the IR-free performance and mass loading targets. Thus, there is some flexibility on the ORR and HER overpotentials providing that the overall overpotential (sum of anode and cathode overpotentials) does not exceed that targeted in the project.

A minimum set of procedures is thus defined to assess the optimised catalyst batches produced on a proper scale for operation under critical conditions relevant to PEM electrolysis application in grid-balancing service. This set of procedures is particularly relevant for the selected class of catalyst formulations.

Description of these methods is reported below. The aim is to produce a data-set table identifying catalyst properties for such specific application.

2.2.1 Catalyst Properties

Catalyst support: In this project, a catalyst support is essentially used only for the cathode catalyst. No support is envisaged for the anode since low catalyst loading can be achieved by using high surface area unsupported oxides and no complications arising from poor support conductivity or stability need to be addressed. On the other hand, a carbon black catalyst support is necessary to achieve a high dispersion of nanosized Pt particles at the cathode and to enhance their stability during operation as well as to reach low Pt mass loadings. However, since the base materials and preparation procedures have already been selected and developed in previous projects, the aim of the present protocols is to assess larger-batch of catalyst as overall and not characterising each component (support phase, catalytic phase). Accordingly, no protocols are here defined for assessing the carbon black support being this already identified from previous projects.

Catalyst properties:

Catalysts properties are assessed in terms of structural, chemistry, morphology and surface characteristics.

Relevant properties are:

- Bulk and surface composition (possibly including depth-profile analysis)
- Crystalline/amorphous structure
- Crystallite size
- Particle size and distribution
- Pore volume, pore size distribution
- Impurities

Measurements are carried out by XRD (structural information, crystallite size from Debye-Scherrer equation, XRF (elemental analysis), TEM (particle size and distribution), SEM-EDX (elemental analysis, morphological, microchemical variations), XPS (surface analysis), BET (pore volume, pore size distribution), ICP (elemental analysis, impurities).

Regarding the impurities, a small aliquot of the catalyst is treated with nitric acid at 80°C for 2 hrs and the solution analysed by ICP to check release of impurities from the catalyst that can affect the electrolysis device.

2.2.2 Electrochemical testing of catalysts

Anode and cathode electro-catalysts: Electrocatalyst testing is directly carried out in single cell using membrane-electrode assemblies in the presence of a reference Aquivion membrane. Recommended cell area for catalyst testing is 5-8 cm² to avoid effects of cell flow fields and mass transport. Reference temperatures 80°C, range from 30°C to 90°C or 140 °C (high temperature testing) in 10°C increments. Water feed rate at the anode 1 g cm⁻² min⁻¹. Reference pressure: 100 kPa. Water quality: $\rho > 5$ MOhm cm. The proposed reference membrane is the extruded E100-09S membrane developed in the frame of ELECTROHYPEM with Aquivion D83-06AX ionomer in the electrodes (base formulation: 67% catalyst and 33% ionomer content in the cathode catalytic layer, 80% catalyst and 20% ionomer content in the cathode catalytic layer) for single cell. The specific amount of ionomer is selected for the catalytic layer from previous studies. This appears to be the best compromise to achieve appropriate ionic and electronic percolation in the catalytic layer as well as to achieve good triple-phase boundary for the electrochemical process in the catalytic functional layer.

The membrane electrode assembly is fabricated using a procedure already optimised for this class of electrocatalysts and Aquivion membrane in Electrohypem. Catalyst-coated membrane (CCM) is obtained by

spray coating of the electrocatalytic inks (formulations defined above) and by hot pressing procedure at 190 °C for 1.5 min at 20 kg cm⁻² preceded by a drying step at 80 °C for 10 min with heating ramp rate of 5 °C min⁻¹.

The current approach differs from the previous project where a pre-screening procedure in liquid electrolyte half cell preceded the catalyst assessment in MEAs. The motivation is that the aims of the HPEM2GAS are not dealing with the screening of new catalyst formulations but just the assessment of the optimised and large scale catalysts batches. Electrocatalyst testing in single cell will allow to carry experiments *in situ* and at temperature and pressure conditions which may be not accessible in half cell. Moreover, these experiments will provide information about catalyst/polymer electrolyte interface performance and stability.

Anode: For diagnostic experiments in single cell dealing with the anode, hydrogen is fed to the cathode which acts both as reference and counter electrode.

In single cell testing, assessment of the anode catalyst (rate determining step) requires the use of a reference electrode system. A simple approach is to feed humidified hydrogen to the cathode which acts both as reference and counter electrode. This avoids that the cathode potential is significantly polarised when the cell is operating at different current densities. In such configuration, the cathode acts both as reference and counter electrode. For diagnostic purposes, the Pt loading at the cathode can be significantly larger (e.g. 2 mg cm⁻²) than the project target (0.1 mg cm⁻²); this to avoid significant polarization of this electrode as required for a reference. Anode polarisation correction for ohmic drop, mainly due to the membrane, using the high frequency intercept in the ac-impedance plots ($E_{a,IR-free} = E_{a,raw} - I \cdot R_u$; with $R_u \equiv$ uncompensated resistance), allows to determine overpotentials at a specific current.

Overpotentials for OER are thus determined at 3 A cm⁻² from IR-free polarisation curves of anodes containing noble metal loading < 0.4 mg cm⁻² at the specific operating temperatures and pressures and reported (**MS2**).

Cathode: Single cell testing of cathode catalysts can be carried out using symmetrical cells with the counter/reference electrode fed with hydrogen and containing large Pt loading as reported above to avoid the reference electrode is polarised. Cathode polarisation correction for ohmic drop, mainly due to the membrane, using the high frequency intercept in the ac-impedance plots ($E_{c,IR-free} = E_{c,raw} + I \cdot R_u$; with $R_u \equiv$ uncompensated resistance), allows to determine overpotentials at a specific current.

Overpotentials for HER are determined at 3 A cm⁻² from IR-free polarisation curves of cathodes containing noble metal loading < 0.1 mg cm⁻² at the specific operating temperatures and pressures and reported (**MS2**).

Overall cathode and anode overpotential: This is the most important procedure to assess the validity of the anode and cathode combination. The polarisation curve is carried out on a MEA using a mass catalyst loading for each electrode as defined in the project (i.e. anode Ir+Ru < 0.4 mg cm⁻², cathode Pt < 0.1 mg cm⁻²), the overall overpotential at fixed current density i.e. 3 A cm⁻² is determined from IR-free curves ($E_{cell,IR-free} = E_{cell,raw} - I \cdot R_u$; with $R_u \equiv$ uncompensated resistance). (**MS2**).

Polarization curves for catalyst assessment (cell voltage vs. current density or I-V): these are carried out in galvanostatic mode i.e. by increasing the current in a logarithm mode (this to allow further data analysis on the basis of the Volmer-Butler equation) and recording the potential once a pseudo steady state-condition (variation < 5 mV/min) is achieved. Alternatively, the current density is varied in steps of 1 min and the voltage recorded at the end of each step. Since an electrolysis cell stabilises very rapidly, this also represents a pseudo steady - state condition. The current density table is essentially the same used for MEA characterisation to avoid discrepancies between the two methods. The current density table is reported in the section of MEA characterisations.

Reference cyclic voltammetry: this is carried out in the potential range 0-1.2 V RHE for the cathode and 0.4-1.4 V RHE for the anode with a sweep rate of 20 mV s⁻¹. Determination of ECSA for the cathode (symmetrical cell, humidified nitrogen is supplied to the working electrode, humidified hydrogen to the reference and counter electrode) is made by integration of H adsorption (theoretically 0.210 mC/real cm²) peaks (0.02-0.4 V RHE) after subtraction of double layer charging at 0.4 V RHE.

For the anode characterisation, a regular cell is used with humidified hydrogen fed to the reference and counter electrode, nitrogen saturated water is supplied to the anode. In this case, the active area expressed as specific charge, q*, is obtained from integration in the entire potential window. This is reported as mC cm⁻² and /or mC mg⁻¹. The voltammetric surface charge is generally considered an indication of the electrochemical active surface area even if a conversion of the charge into surface area is difficult because the nature of the surface reactions is not known precisely.

Accelerated stress tests: Anode catalyst degradation with specific regard to its assessment for operation in grid-balancing service is investigated by accelerated tests consisting of electrolysis cell potential holding at the high potential of 2.2 V vs. RHE for 48 h. This test can be repeated several times with electrode/cell diagnostics (see below) carried out between two consecutive cycles to monitor the evaluation of critical parameters such as Tafel slope, electrochemical active surface area, polarisation resistance etc.

A second test deals with potentiodynamic cycling of the anode in a driven mode cell between 1.4 and 2.2 V RHE (sweep rate 150 mV s⁻¹) in 10⁴ cycles.

Cathode catalyst degradation is investigated by accelerated tests consisting of electrolysis cell potential holding at 2.2 V for 48 h as well as by using potentiodynamic cycling of the cathode in a symmetrical cell between -0.5 V and 0 V RHE (sweep rate 150 mV s⁻¹) in 10⁴ cycles.

Ex-situ physico chemical analysis: Pre- and post-operation physico-chemical analyses of the catalysts are carried out by XRD (structural information, crystallite size from Debye-Scherrer equation), XRF (elemental analysis), TEM (particle size and distribution), SEM-EDX (morphological, micro-chemical variations), XPS (surface analysis).

2.3 Membrane-electrode assembly assessment

The role of the membrane-electrode assembly in a PEM electrolyser has been described above. Determination of the fundamental properties for the MEA is a pre-requisite to understand stack and system behaviour.

The main targeted improvements indicated in HPEM2GAS for the membrane-electrode assemblies are dealing with:

- Reduction of the anode and cathode *noble metal catalyst loadings* (anode Ir+Ru < 0.4 mg cm⁻², cathode Pt < 0.1 mg cm⁻²).
- Demonstrate long-lifetime potential with single cell MEA having a *degradation rate* of < 5 μV/h;
- Enhance performance of large area (≥ 415 cm²) MEAs to achieve suitable *efficiency* characteristics for the entire device and to allow for a direct reduction of capital costs;
- Achieve a current density of 3 A cm⁻² at 1.8 V/cell and 4.5 A cm⁻² at E_{Cell} < 2 V.

A set of measurement procedures is defined to assess the progress obtained for the membrane-electrode assemblies with particular regard to the achievement of these targets. These procedures deal with determination of mass loading of catalysts, performance, efficiency, stability, capability to sustain duty cycles for

the specific application of this project. MEA testing in this project is addressed to the materials that have been down-selected from previous projects. The set of protocols are presented below.

2.3.1 Determination of the catalyst loading for MEAs

Determination of the catalyst loading for MEAs (MS3): A catalyst coated membrane approach is conventionally used. Thus, catalysts are directly deposited onto the membrane, e.g. by spray coating. Determination of the catalyst content is carried out by weighting 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 weighting.

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 series, as those used in catalyst assessment experiments, an 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.

2.3.2 Cell area and operating conditions

Cell area and operating conditions: MEA screening is first carried out in a small single cell (3, 5 or 25 cm² geometrical area) and thereafter the optimised MEA is assessed in a large area cell (nominal geometrical area cell for this project is 415 cm²). The flow field design for the small single cell is singled out from previous projects whereas the large area cell specific of this project is designed by ITM.

Reference temperatures for MEA assessing is 80°C, the temperature range vary from 30°C to 90°C or 140°C (high temperature testing) in 10°C increments. Reference water feed rate at the anode is fixed to 1 g cm⁻² min⁻¹.

Reference pressures are: 1 bar abs for low pressure studies, 30 bar_{Abs} or 80 bar_{Abs} for high pressure experiments.

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

MEA conditioning: MEA is installed in a single cell and equilibrated at 80°C with de-aerated distilled water ($\rho > 5$ MOhm cm) fed to both compartments at ambient pressure, pre-heated to this same temperature at a flow rate of 1 g cm⁻² min⁻¹.

MEA conditioning is made under 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.

2.3.3 Cell performance

Cell Performance (cell voltage at specific current density): MEA polarisation curves

Polarisation curves under reference operating conditions: 80°C, P=1 bar_{Abs}

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. The motivation 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. 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 polarisation curve can be measured as single sweep or, preferably, as two sweeps by increasing current followed by decreasing current to individuate any hysteresis. 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:

| 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 | |
| 0.3 | |
| 0.35 | |
| 0.4 | |
| 0.45 | |
| 0.5 | |
| 0.6 | |
| 0.7 | |
| 0.8 | |
| 0.9 | |
| 1 | |

| Current Density [A·cm⁻²] | Cell Voltage [V] |
|--|-----------------------------------|
| 1.1 | |
| 1.2 | |
| 1.3 | |
| 1.4 | |
| 1.5 | |
| 1.6 | |
| 1.7 | |
| 1.8 | |
| 1.9 | |
| 2 | |
| 2.2 | |
| 2.4 | |
| 2.6 | |
| 2.8 | |
| 2.9 | |
| 3.0 | |
| 3.2 | |
| 3.4 | |
| 3.6 | |
| 3.8 | |
| 4.0 | |
| 4.2 | |
| 4.5 | |
| 5 | |

A typical example of polarisation curves recording according to this method, at different temperatures with 2 V as cut-off voltage is reported in Fig. 1.

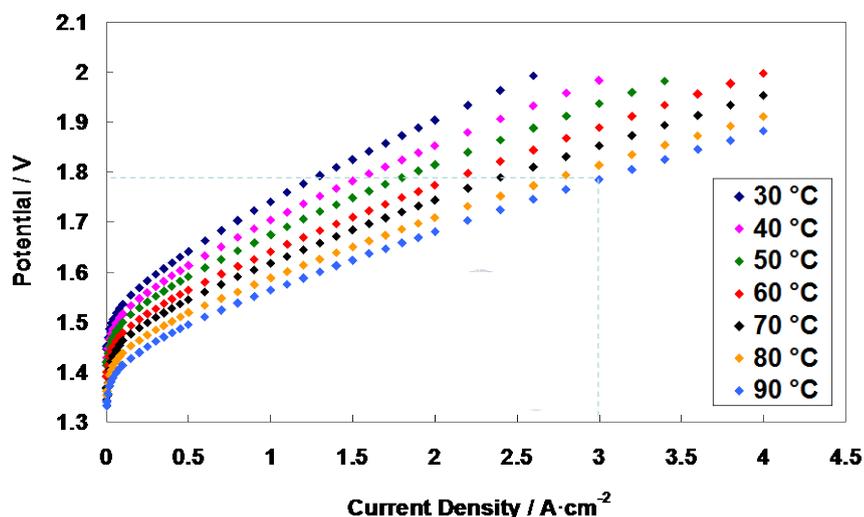


Figure 1– Example of MEA polarisation curves at different operation temperatures and ambient pressure

The polarisation curve carried out on a MEA, using a total noble metal catalyst loading $<0.5 \text{ mg cm}^{-2}$, allows to assess MEA performance at the specific operating temperature and pressure. The terminal cell potentials at fixed current densities of 3 A cm^{-2} and 4.5 A cm^{-2} are determined from polarisation curves and reported (**MS3**).

For a cell test at a fixed cell temperature, water inlet temperature must be maintained at the same water outlet temperature that represents the cell temperature. The presence of pressure vessels in high-pressure cells impedes, in some cases, a direct measurement of the cell temperature close to the MEA. This can be carried out any way in the case of a low-pressure single cell.

The current density is preferably increased to the maximum achievable current with a *cut-off voltage* of 2.0 V. The sampling rate should be in the range 1-0.1 Hz. The cell voltage at a given (averaged) current density is averaged over the last 1 min of measurements and plotted against the current density. At the end of the I-V curve measurements, the current density is be set to zero (OCV) at ambient pressure before stopping all the testing equipment.

Polarisation curves under specific operating conditions:

-Influence of the cell temperature: by maintaining constant feed of the water feed and water quality as above, repeat the I-V curve measurements at increasing temperatures from RT or 30° to 90°C (in steps of 10-20°C). The isothermal condition (no temperature variation at different current densities) must be established by using heating/cooling devices for the water recirculating. Water recirculation thus acts as a thermostating fluid. The cell temperature should be stabilised under OCV for a minimum of 20 minutes before proceeding with the next I-V curve measurement.

- Influence of pressure and cell temperature under pressurised mode: the maximum temperature could be increased up to 140°C under pressurised mode (in steps of 10-20°C) whereas pressure can be increased up to 80

bar_{Abs}. Reference pressures are 1 bar_{Abs}, 30 bar_{Abs}, 80 bar_{Abs}. Increase the pressure to 5 bar_{Abs} and further steps of 5/10 bar.

Two modalities can be investigated; differential pressure (pressurised cathode) and constant pressure (the latter will be applied only for pressures lower than 15 bar to avoid Ti hardware reaction with pressurised oxygen at the anode).

2.3.4 Cell stability

Cell Stability (cell voltage variation as function of time at specific current density or in duty cycle tests)

Durability studies: Steady-state galvanostatic operation at 1 A cm⁻² and 3 A cm⁻² for at least 1000 hrs under specific temperature and pressure conditions. Cell conditioning, water feed, selected cell hardware as above. Data logging is at a frequency of 10⁻² Hz.

Reference polarization curve and ac-impedance spectroscopy at the beginning and at the end of the experiment. Post-operation ex-situ analyses by XRD, TEM, SEM-EDX and XPS.

A typical example of durability test recording according to this method at specific temperature and current density is reported in Fig. 2.

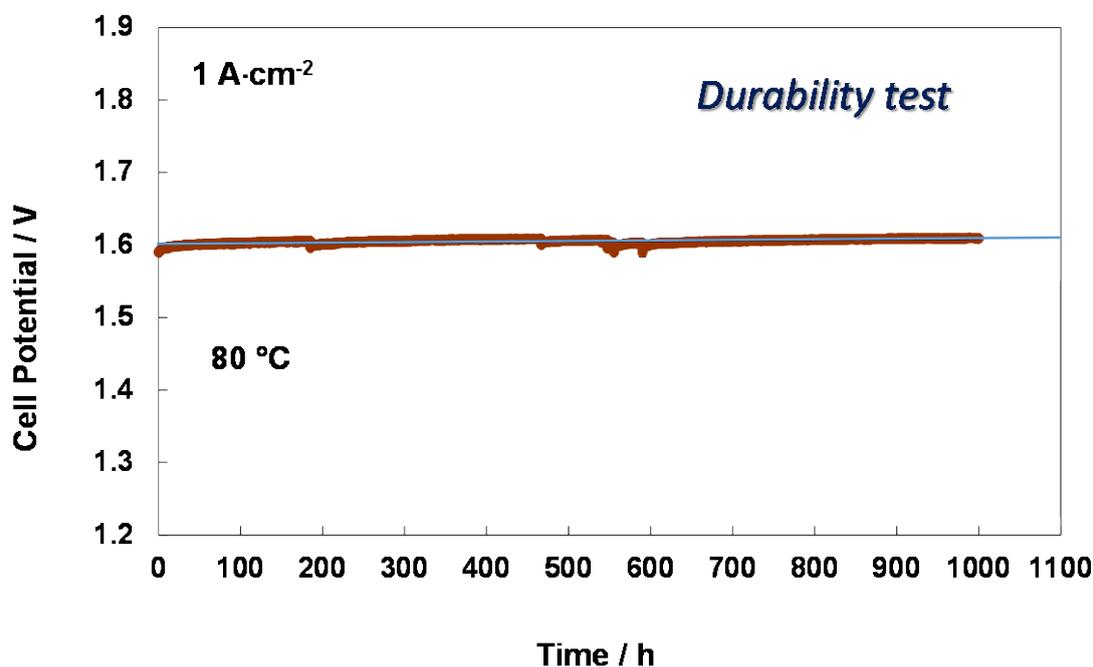


Figure 2– Example of MEA durability test at specific temperature and constant operating current density

Accelerated stress tests: Specific accelerated stress tests consist in a high potential hold tests and dynamic cycling. These tests, if carried out in a wide temperature range, can provide information on the capability of the MEA to address grid-service.

MEA Accelerated Stationary Test A potential hold test consists in 48 hrs potential hold at 2.2 V at relevant temperature and pressure operation conditions. Water feed, temperature and pressure as above. This test can be repeated several times with cell diagnostics (see below) carried out between two consecutive cycles to monitor the evaluation of critical parameters such as performance in I-V curves, high frequency resistance, polarisation resistance, gas crossover etc. During diagnostics experiments there is no need to modify temperature and pressure and possibly no cell shut-down procedure is necessary.

MEA Accelerated Cycling Test: MEAs are tested under a load cycle at constant temperature and pressure to test degradation mechanisms occurring under a dynamic load as occurs in grid-balancing service. The specific test procedure is described below:

AST protocol for MEAs

| | |
|---|--|
| Cell Conditioning | Refer to <i>MEA conditioning described above</i> |
| Test Conditions | <p>Single cell 5 – 415 cm²</p> <ol style="list-style-type: none"> 1. Before starting test operate for 24 hrs at steady-state, 1A/cm². 2. Measure an IV curve as detailed in the Measurement of Current-Voltage Polarisation Curve Procedure (Current Range: 0.5 mA/cm² – 5 A/cm²; cut-off 2.2 V) and make ac-impedance analysis as described in the text. 3. Followed by a 6 step cycle: <ul style="list-style-type: none"> • Step 1: 10 seconds at 0.15 A/cm² (5% load) • Step 2: 10 seconds at 3 A/cm² (100% load) • Step 3: 10 seconds at 4.5 A/cm² (150% load) • Step 4: 10 seconds at 3 A/cm² • Step 5: 10 seconds at 0.15 A/cm² • Step 6: 10 seconds at 0 A/cm² (only if operating pressure is ambient pressure) • Repeat this test 1500 times to form a first set of AST (corresponding to 25 h) 4. At the end of each set of AST (1500 cycles, 25 h), measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm² – 5 A/cm²; cut-off 2.2 V) and carry an ac-impedance test. |
| Number of Cycles | 5 sets of 1500 cycles (7500 cycles corresponding to 125 hrs dynamic operation with 5 cell diagnostic intervals) |
| Cut-off voltage in this procedure is set to 2.2 V | |

Performance decay is measured as percentage (%) voltage increase vs. number of cycles from polarisation curves at 3 A cm⁻²

This procedure takes into account the specific targets of the HPEM2GAS project. The HPEM2GAS DoA reports a Partial load operation, from 5% to ~160% and a nominal operating current of 3 A cm⁻² (100% load). Each time-step is not significantly different than wind energy power spikes occurring with a frequency of 1 - 2 Hz and similar to photovoltaic power fluctuations (typically in the range of 0.5-0.1 Hz). The time associated to each step is, in any case, larger than the time response of current power electronics.

2.3.5 Cell diagnostics

Cell diagnostics: *ac-impedance analysis, gas crossover, electrochemical surface area*

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 100 mA cm⁻², 3 A cm⁻² and the maximum achieved current. In the potentiostatic mode, apply 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. 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.

Crossover measurements: these are carried out *in-situ* under relevant temperature and pressure conditions by using the sensor method or by electrochemical methods in driven mode if applicable.

Electrochemical hydrogen crossover test is carried out according to the procedure reported below:

Specifically for crossover measurements, flow 100% humidified hydrogen on Ir-Ru oxide electrode (equiv. of 1.5 stoich at 1 A/cm²), flow humidified inert gas at the Pt electrode; humidification is necessary to keep membrane hydrated. Use Pt as working electrode. Sweep working electrode potential from rest potential (100 mV) to 400 mV against counter-reference electrode at 2 mV/s – current limited by crossover rate from anode to cathode. Crossover rate reported at 400 mV (1 mA/cm² ≈ 0.070 ml/min/cm² hydrogen) under steady state.

Possibly measure as a function of temperature, ΔP, humidity, thickness.

Electrochemical active surface area (in-situ ECSA) determination:

This was already discussed in the catalyst section. In general, this test is not only useful for catalyst assessment but also for the assessment of the electrode-electrolyte interface including degradation phenomena that may occur during stability studies or accelerated stress-tests.

Reference cyclic voltammetry for the anode is carried out as specified above by feeding 100% humidified H₂ at the reference/counter electrode (equiv. of 1.5 stoich at 1 A/cm²). Nitrogen saturated water is supplied to the working electrode. The dew-point temperature is equal to cell temperature. It is preferable to use a floating reference electrode exposed to the humidified electrode.

For the Pt electrode, the CV is carried out in the potential range 0-1.2 V RHE and between 0.4-1.4 V RHE for the Ir-Ru oxide electrode with a sweep rate of 20 mV s⁻¹. Determination of ECSA for the Pt cathode is made by integration of H adsorption (theoretically 0.210 mC/real cm²) peaks (0.02-0.4 V RHE) after subtraction of double layer charging at 0.4 V RHE.

For the Ir-Ru oxide anode, active area is expressed as specific charge, q^* , that is obtained from integration in the entire potential window. This is reported as mC cm^{-2} and /or mC mg^{-1} .

2.3.6 Data treatment

Electrocatalyst performance evaluation: Overall overpotential is measured at 1 and 3 A cm^{-2} under relevant temperature and pressure conditions from IR-free Tafel plots in the presence of specific metal loading (e.g. total noble metal loading 0.5 mg cm^{-2}).

Ohmic resistance: this is determined from the high frequency intercept on the real axis of the Nyquist plot obtained from AC-impedance spectroscopy. This can be subtracted to the cell hardware resistance measured without the MEA and may be indicative of membrane conductivity under relevant operating conditions.

MEA performance evaluation:

Cell potential is determined at 1 and 3 A cm^{-2} under relevant temperature and pressure conditions.

Voltage efficiency: this is the ratio between the thermoneutral potential and operating potential and varies as a function of the current density.

$$\eta_v \% = [E_{\text{thermoneutral}} / E_{\text{cell}}] \cdot 100$$

Faradaic efficiency: this is the ratio between the hydrogen effectively produced (measured by gas chromatographic analysis) and that theoretically produced from the Faraday law at specific current density (I).

$$\eta_i \% = [\dot{n}_{\text{H}_2} \cdot 2F / I] \cdot 100$$

This can vary as a function of the current density (I). It can be also evaluated from crossover data.

Overall MEA efficiency: this is the product of voltage efficiency and current efficiency and varies with the current density.

$$\eta \% = \eta_v \% \cdot \eta_i \%$$

MEA durability:

- *Stationary:* Cell voltage decay determined by curve fitting in the entire time window (≥ 1000 hrs) of the stationary test at 1 and 3 A cm^{-2} excluding the first 100 hrs of cell conditioning.

If shut-down and start-up cycles are carried out during the stationary test, the final cell recording cannot be made in an time interval that is less than 100 hrs from the last start up event. Voltage increase due to cell degradation is expressed in $\mu\text{V/h}$.

- *Dynamic and Accelerated stress tests:* Cell voltage increase associated to cell decay is determined from polarisation curves measured before and after the accelerated stress tests and measured at 1 and 3 A cm^{-2} . Performance decay is reported as % loss of voltage efficiency at the specific currents.

3 Definition of a set of protocols and data treatment for assessing PEM Electrolysis Stacks

The objective of this section is to define characterisation and test protocols for the assessment of performance, efficiency and durability of PEM water electrolyser stacks developed in HPEM2GAS. Short stacks are tested in dedicated test stations and final stack is tested inside the system which acts as a test station. The procedures and methods defined within are a set of protocols for the electrochemical characterization under the specific operating conditions applicable to both stationary and grid-balancing service.

The protocols include electrochemical polarization curves at the beginning of test (BoT) and end of test (EoT) to determine important parameters such as performance, efficiency and voltage decay (performance loss). The specific procedure includes constant load (current) operation, and dynamic load operation with a specific current profile to simulate at various steps the situation occurring under grid-balancing service operation. Electrochemical impedance spectroscopy (EIS), gas crossover and water analysis are used for in-situ diagnostics and EoT characterisation. Ex-situ tests, performed after stack disassembly, are used to assess degradation mechanisms. Protocols for non active components assessment are just briefly included since these have been treated in previous projects.

The set of protocols is organised as follows:

1) Protocols for assessment of stack housing components:

These mainly concern with bipolar plates, backing layers and current collectors of PEM electrolyser stack housing. Essentially, these consist in measuring variation in contact resistance before and after duty cycle testing.

2) Definition of protocols and procedures for initial stack assessment

These are similar to the MEA testing protocols described above and concern with durability tests, using polarisation as a key indicator of performance loss.

The stacks are initially assessed under stationary conditions.

Durability is assessed by investigation of voltage increase at constant current operation under specific conditions of temperature and pressure.

3) Tests and protocols for assessment the stack dynamic behaviour

These procedures are aiming to investigate the capability of the stack to sustain randomly occurring harsh conditions such as high cell potentials, load cycles, start-up / shut-down cycles. Accordingly, the stacks are tested under various conditions including load cycle at constant temperature and pressure to test degradation mechanisms occurring under a dynamic load.

4) Protocols for stack failure analysis

Diagnostic procedures regard the determination of important parameters. These essentially use ac-impedance measurements, cyclic voltammetry of single cells within the stack and ex-situ, analysis of the

water and crossover measurements. Physico-chemical analysis of the active components is also to be performed post-operation.

3.1 Protocols for assessment of stack housing components

Stack housing is essentially composed by bipolar plates, diffusion layers, sealing gaskets. These are often defined non active components since are not directly involved in the primary electrochemical process but they contribute to determine performance and stability since distribute electrical energy and reactant over the active parts and collect reaction products. The assessment procedure is essentially involving post-operation physico-chemical analysis of non-active stack components to assess any degradation effects related with operation under practical conditions. These are subjected to physico-chemical studies after prolonged operation in short-stacks in order to verify if the optimised materials and configurations can apply for the full stack operating inside the electrolysis system.

3.1.1 Physico-chemical characterisation of stack components

Pre- and post-operation physico-chemical analyses deal with elemental (XRF), structure (grazing angle XRD), microchemical and morphological (SEM-EDX), surface (XPS) analysis of altered or corroded parts.

Electronic conductivity of bipolar plates and current collectors before and after the stack testing is determined by measuring the difference in resistance between a four-point probe method and a two point contact method. The procedures for physico-chemical experiments are the conventional ones; thus, such protocols have not been detailed here.

Conductivity test protocols are defined in the following.

3.1.2 Measurement of in-Plane Electrical Conductivity

This is performed using controlled current electrochemical impedance spectroscopy (EIS). Low frequency measurement is not necessary and measurements can be carried out from the maximum frequency (50 kHz down to 1 Hz with data log 5 points per decade).

Measurement of In-Plane Conductivity

Protocol and Metrics

| | |
|------------------------------|---|
| Pre-conditioning | No specific procedures |
| Operating conditions: | |
| Measurement technique | Potentiostatic Electrochemical Impedance Spectroscopy (EIS) |
| Component size | As appropriate (but must be recorded) |
| Technique | Four point probe/two point probe |
| Frequency range | 50 kHz to 1 Hz (5 steps/decade) |
| DC current | no DC current |
| AC voltage | 10 mV |

| | | |
|---------------------------------------|--|--------------------------|
| Analysis | <ul style="list-style-type: none"> Plot each result in standard Nyquist form Where the signal first crosses the real axis is the series resistance (high frequency resistance) Contact resistance is $\frac{1}{2}$ the difference between the two point resistance and the four point resistance (voltage probes must be at same point, thickness and under the same applied pressure. | |
| METRIC | FREQUENCY | TARGET |
| <i>Nyquist plot</i> | Start and end of any test plus as required | |
| <i>Electronic conductivity</i> | As required | No target for monitoring |

3.2 Definition of protocols and procedures for initial stack assessment

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

The nominal rated hydrogen production capacity is planned in 80 (nominal)-140 (transient) kg H₂/day.

The planned stack active area is 415 cm² and the number of cells is equal to 75 cells (**MS4**) in order to reach the nominal capacity at the targeted operating current densities.

The active area results from an analysis of the benefits in reducing capital costs and the need to reduce mechanical stresses for high pressure operation as well as temperature gradients at high currents.

Short stack testing is carried out under controlled conditions in designed test stations operating at specific temperatures and pressures whereas the full stack is assessed directly in the balance-of-plant.

3.2.1 Performance assessment from stack Current-Voltage Polarization Curve

This is a measure of the stack voltage as a function of the applied current. The current is raised and then lowered to measure any hysteresis. Voltage related to specific cells or a set of cells can be monitored. The results are analysed to determine energy consumption of the stack and efficiency at the nominal capacity. Energy consumption is reported in terms of kWh/ kg H₂ and efficiency is referred to the HHV of H₂; beside this, the average cell voltage at a specific current density of 1, 3 and 4.5 A cm⁻² will provide a comparison of stack performance with single cell MEA testing.

Measurement of Stack Current-Voltage Polarization Curve is reported below:

Stack I-V Curve

Protocol and Metrics

| | |
|-------------------------|---|
| Pre-conditioning | Stack MEAs must be hydrated prior to measurement It is recommended that stack run for at least 24 hours to ensure the MEAs have reached a steady state |
|-------------------------|---|

Operating conditions:

| | |
|---|---|
| Control | Chronopotentiometric (current controlled; voltage recorded) |
| Cell size/number of cells/ series connection | As appropriate for short stack; 75 cells, 415 cm ² for full stack |
| Water temperature | Recorded on both exits and reported with I-V curve |
| Pressure | Pressure must remain at atmospheric pressure for currents less than 0.4 A·cm ⁻² . Higher pressures can be used above this current density but must be recorded and reported. |

Current Density range 2 mA·cm⁻² to 4.5 A·cm⁻² (and reversed)

Step size Smaller at low currents such that the change in voltage between step size is < 30 mV/cell (see example below)

Voltage monitoring Monitoring of terminal stack voltage and each single cell voltage

Technique

- Hold current at 100 mA·cm⁻² for 5 minutes to ensure catalysts are in the correct oxidation state
- Step current to 2 mA·cm⁻²
- Record voltage after 1 min (Note: if dV/dt > 1 mV·cell⁻¹·cm⁻²·s⁻¹ then must wait until dV/dt < 1 mV·cell⁻¹·cm⁻²·s⁻¹ before recording voltage)
- Step to next current and repeat .

Single cell voltage cut off 2.2 V /cell

| METRIC | FREQUENCY | TARGET |
|--------|-----------|--------|
|--------|-----------|--------|

| | | |
|------------------|--|--|
| I-V curve | Start and end of any test plus as required | |
|------------------|--|--|

| | |
|--|--|
| Energy consumption (pseudo steady state test) | < 48 kWh/kg H ₂ at 80 kg H ₂ /day. |
|--|--|

| | |
|--|---|
| Efficiency (pseudo steady state test) | > 82% vs. HHV of H ₂ at 3 A cm ⁻² current density |
|--|---|

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

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

Set of applied current densities for the stack against which voltage should be recorded:

| Current Density [A·cm ⁻²] | Terminal stack Voltage [V] | Average Cell Voltage [V/cell] | Current Density [A·cm ⁻²] | Terminal stack Voltage [V] | Average Cell Voltage [V/cell] |
|--|-------------------------------|----------------------------------|--|-------------------------------|----------------------------------|
| 0.002 | | | 1.2 | | |
| 0.01 | | | 1.4 | | |
| 0.06 | | | 1.6 | | |

| | | | | | |
|-----|--|--|-----|--|--|
| 0.1 | | | 1.8 | | |
| 0.2 | | | 2 | | |
| 0.3 | | | 2.5 | | |
| 0.4 | | | 3.0 | | |
| 0.6 | | | 3.5 | | |
| 0.8 | | | 4.0 | | |
| 1.0 | | | 4.5 | | |

Note: water temperature and pressure should be controlled and recorded.

The polarisation curve is carried out on a full stack (75 cells, 415 cm² area). The average cell potential at a fixed current densities of 3 A cm⁻² is determined from the polarisation curves and reported. (MS4).

3.2.2 Stack stability assessment under stationary conditions

The stack stability assessment under stationary conditions consists in a Stack steady-State Test of 1000 hrs at 3.0 A/cm² and the determination of the stack voltage and efficiency at the nominal capacity.

Stack is tested under constant load, temperature and pressure, to measure the decay rate at 3 A/cm².

Stack steady-State Test at 3 A/cm² Protocol and Metrics

| | |
|---------------------------|--|
| Stack Conditioning | Refer to MEA conditioning Procedure |
| Test Conditions | Short-stack or Stack of nominal capacity <ol style="list-style-type: none"> 1. Before starting test, operate for 24 hrs at steady-state, 1.0 A/cm² for conditioning. 2. Measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Curve Procedure (Current Range: 2 mA/cm² – 4.5 A/cm²). 3. Operate the stack at a steady-state 3.0 A/cm². 4. At the end of the test, measure an I-V curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 2 mA/cm² – 4.5 A/cm²). |
| Total Time | 1000 hrs after measurement of the first I-V curve |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |

| METRIC | FREQUENCY | TARGET |
|---|---|--------------------------|
| F⁻ release or equivalent for non-fluorine membranes | Every 100 hrs of steady-state operation from the beginning of the test. | No target for monitoring |
| Metallic ions release / increase of water conductivity at stack outlet | After 100 hrs of steady-state operation from the beginning of the test. | No target for monitoring |

| | | |
|-------------------------------------|--|--|
| Hydrogen Crossover | Continuously monitored. Systems should be put in place to shut down should the levels go above ½ the flammability limit. | H ₂ concentration in the oxygen stream <0.5 vol.% at specific pressure and current |
| Voltage Degradation | 1000 hrs of operation after first I-V curve. | ≤ 5 μV/hr degradation in operating voltage using line of best fit and excluding the first 100 hrs of conditioning. |
| I-V Curve | BoT and EoT | No target for monitoring |
| Determine hydrogen flow rate | Every 100 hrs | |
| Energy consumption or | | < 48 kWh/kg H ₂ at a production rate of 80 kg H ₂ /day. |
| Efficiency | | > 82% vs. HHV of H ₂ at 3 A cm ⁻² current density |

The time-test curve is carried out on a full stack (75 cells, 415 cm² area) at a fixed current densities of 3 A cm⁻². Degradation in average cell potential is determined from a 1000 hrs time-test using line of best fit and excluding the first 100 hrs of conditioning and reported. **(MS4)**.

3.3 Tests and protocols for an assessment of the stack dynamic behaviour

Procedures are here defined to examine and assess the stability of the stack and stack components under randomly occurring harsh conditions such as high cell potentials, load cycles, load on-off, etc. these effects are quantified in terms of performance decay.

3.3.1 Stack Cycling Test

Stack is tested under a load cycle at constant temperature and pressure to test degradation mechanisms occurring under a dynamic load. This procedure may also include a combined load-pressure cycling.

Stack Cycling Test Protocol and Metrics

| | |
|---------------------------|---|
| Stack Conditioning | Refer to MEA Conditioning/Hydration Procedure |
| Test Conditions | <p>Short stacks and Stack of nominal capacity</p> <ol style="list-style-type: none"> 1. Before starting test operate for 24 hrs at steady-state, 1A/cm². 2. Measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Polarisation Curve Procedure (Current Range: 2 mA/cm² – 5 A/cm²; cut-off voltage 2.2 V/cell). 3. Followed by a 5 or 6 step cycle: <ul style="list-style-type: none"> • Step 1: 10 seconds at 0.15 A/cm² (5% load) • Step 2: 10 seconds at 3 A/cm² (100% load) • Step 3: 10 seconds at 4.5 A/cm² (150% load) • Step 4: 10 seconds at 3 A/cm² |

- Step 5: 10 seconds at 0.15 A/cm²
 - Step 6: Optional 10 seconds at 0 A/cm² (after decreasing operating pressure to ambient pressure); this step also includes a pressure cycle.
 - Repeat this test 1500 times to form a first set of AST (corresponding to t≈21 or 25 h depending on how many steps 5 or 6)
4. At the end of each set of AST (1500 cycles, t≈21 or 25 h), measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Curve Procedure (Current Range: 2 mA/cm² – 5 A/cm²; cut-off 2.2 V).

| | |
|-------------------------|---|
| Number of Cycles | 5 sets of 1500 cycles (7500 cycles corresponding to ~105-125 hrs dynamic operation with 5 stack diagnostic intervals) |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |
| | Cut-off voltage in this procedure is set to 2.2 V |

| METRIC | FREQUENCY | TARGET |
|---|------------------------------|--|
| F⁻ release or equivalent for non-fluorine membranes | BoT and EoT | No target for monitoring |
| Hydrogen Crossover | BoT Following 1500 cycles | H ₂ concentration in the oxygen stream <0.5 vol.% at recorded pressures and current |
| IV Curve | BoT Following 1500 cycles | Low voltage decay in line with steady state tests |

Performance decay is measured as percentage (%) voltage increase vs. number of cycles from polarisation curves at 3 A cm⁻²

This procedure takes into account the specific targets of the HPEM2GAS project as reported in the DoA i.e. a partial load operation, from 5% to 150-160% and a nominal operating current of 3 A cm⁻² (100% load). Each step time is not significantly different than typical wind energy power spikes occurring with a frequency of 1 - 2 Hz and similar to photovoltaic power fluctuations (typically in the range of 0.5-0.1 Hz). The time associated to each step is, in any case, larger than the time response of current power electronics.

3.4 Protocols for stack failure analysis

Specific cells (e.g. terminal cells, middle position cells) and/or group of cells are monitored during stack operation in order to get information on stack sections. Electrochemical diagnostics such as in-situ cyclic voltammetry and ac-impedance analyses are used to determine voltammetric charge, series resistance, polarization resistance and double layer capacitance for different cells in the stack. By using proper electrochemical set-up for diagnostic purposes, these techniques may be applied also with large geometrical area MEAs in the stack. These methodologies allow to monitor the eventual differences in the operating behaviour of the different MEAs of the stack during operation.

AC-impedance is carried out in galvanostatic or potentiostatic mode according to the procedure described for the MEA. Galvanostatic mode is the only option when the ac-impedance spectra are carried out under specific load, e.g. at 3 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 in the Nyquist plot), whereas polarization resistance is determined from the low frequency intercept. In the potentiostatic mode, the cell voltage is fixed at 1.5 V/cell in order to compare the data-set to those 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).

Reference cyclic voltammetry is to be carried out according to the procedures defined for MEA testing. This experiment is carried out in the driven mode by feeding nitrogen saturated water to the working electrode and 100% humidified H_2 to the counter/reference electrode. CVs are carried out in the potential range 0-1.2 V RHE for the cathode and 0.4-1.4 V RHE for the anode with a sweep rate in the range $20\text{-}150 \text{ mV s}^{-1}$. The proper sweep rate will be selected to avoid current overload depending on the active cell area in the stack. Determination of ECSA for the cathode is made by integration of H adsorption (theoretically $0.210 \text{ mC/real cm}^2$) peaks (0.02-0.4 V RHE) after subtraction of double layer charging at 0.4 V RHE; whereas for the anode, active area, expressed as specific charge q^* , is obtained from integration in the entire potential window.

Protocols for *in-situ* crossover measurements of gases under practical operation include sensor methods and electrochemical methods (H_2). Details of these operating procedures are reported in the MEA testing section.

A post-operation physico-chemical analysis can be carried out on active (membrane, catalysts, MEAs) to individuate any degradation effect related with operation under practical stack configuration with respect to the single cell MEA testing. 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).

4 Tests and protocols for electrolysis system assessment under nominal operation and validation for grid-balancing service

4.1 Protocols for assessing the electrolysis system under nominal operation

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

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 H₂-water separation. Separate studies carried out at short stack level concerning with the effects of water contaminants form the basis for the optimization of the ion exchange cartridges for the system.

The power conditioning/controls unit is the component of the electrolysis system that primarily address the effect the grid fluctuations but also the other sub-units must be designed to support the requested dynamic behaviour. An important example is regarding the ion exchange resin. This component needs to sustain a significant increase of the water temperature at the stack outlet during operation with a load significantly larger than the nominal one. In fact, a wide range of operation capacity is planned for the PEM electrolysis system developed in HPEM2GAS (up to 150-160% of the nominal load).

The system is first assessed under stationary conditions to verify if it can reach the relevant targets in terms of performance, efficiency, stability associated to the HPEM2GAS objectives and milestones.

Validation of nominal hydrogen production capacity and system efficiency

System operation under stationary conditions

Protocol and Metrics

| | |
|-----------------------------------|---|
| Operational capacity range | <ul style="list-style-type: none">Nominal capacity: 80 kg H₂/day |
| System Conditioning | Operate the system at ~30% of nominal capacity and for sufficient time (24 hrs) to guarantee appropriate stack/sub-systems conditioning. |
| Test Conditions | System of nominal capacity <ol style="list-style-type: none">Operate the system with a constant electric power input of 180 kW and nominal temperature and pressure for 100 hrs (steady-state)Determine the average hydrogen production rateShut-off the system |
| Number of Cycles | Set as required |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |

| METRIC | FREQUENCY | TARGET |
|---------------------------------|-------------|--|
| Hydrogen production rate | BoT and EoT | > 80 kg H ₂ /day at 180 kW |
| Energy consumption / Efficiency | BoT and EoT | <48 kWh/kg H ₂ or >82% vs. HHV at 80 kg H ₂ /day |
| Hydrogen quality | BoT and EoT | 5 N |

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

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

The PEM electrolysis system is tested with constant 180 kW power input for 100 hrs. Hydrogen production capacity, efficiency related to HHV H₂ and energy consumption per kg H₂ of produced hydrogen are determined and reported. (MS5)

4.2 Grid-balancing service

Electrical grids sharing a significant fraction of renewable energy sources (RES) require storage technologies such as hydrogen production from water electrolysis to address the congestion of transmission, to provide stabilization from frequent fluctuations as well as to manage load shifting, peak shaving and to enhance power quality.

Conventional electrolyzers are generally designed to operate continuously at their nominal capacity by supplying the system with a constant power from the grid (stationary condition). However, the main advantage of a grid-connected application is to provide grid-balancing service. In this regard, it is necessary that the advanced electrolysis systems are provided with a dynamic range of operational capacity and proper dynamic characteristics to address instabilities related to the renewable energy share thus contributing to the power regulation and stabilisation of the grid. The dynamic behaviour in particular regards fast response, cold start, ramp rates.

Thus, it is very appropriate to define protocols for a basic assessment of the capability of the complete electrolysis system to operate properly for grid-service. These protocols are essentially related to current profiles (waveforms) simulating intermittent conditions in terms of load, cold and warm start-up.

The effects caused on the grid by intermittent operation of renewable energy sources reflect on the PEM electrolysis system operation while it is performing a grid balancing service. This causes a corresponding performance decay of the electrolysis system, in particular the main effect is on the stack but also other system components are strongly affected. As above discussed, the protocols here individuated to assess the capability of the system to support such operating conditions concern with load and on-off cycles, using specific current

profiles simulating the behaviour of a grid sharing a large amount of renewable power sources, especially wind-mills, as planned in the HPEM2GAS project. An assessment of the properties of the PEM electrolysis system in relation to such operating conditions is thus a good indication of its characteristics for operation in grid-balancing service applications.

4.3 Protocols for assessing the PEM electrolysis system for operation under grid-balancing service

The protocols are addressed to validate the system characteristics in order to allow time-response of less than a few seconds for a change from 5 to 100% of full operational capacity and to increase the coupling efficiency of the PEM electrolyser with the grid. A large dynamic range of operational capacity (5-160%) allows an appropriate coupling of the system with a large variation of input power or gas output requirements as it occurs with grids sharing large amounts of wind, solar energy.

Procedures aimed to evaluate the effect of ripple current can be identified successively to the experimentation.

4.3.1 Operational capacity

The system is assessed to verify if it can reach the HPEM2GAS targets in terms of operational capacity range. This is an important characteristic for grid-service since it is expected that the system can operate under reduced or increased load.

The following test is addressed to assess the PEM electrolyser load range:

Validation operational capacity range

| System operation under stationary conditions Protocol and Metrics | |
|--|---|
| Operational capacity range | <ul style="list-style-type: none"> Nominal capacity: 80 kg H₂/day Upper operational capacity: 140 kg H₂/day (transient) Lower operational capacity: 4 kg H₂/day |
| System Conditioning | Operate the system at ~50% of nominal capacity and for sufficient time (4 hrs) to guarantee appropriate stack/sub-systems conditioning. |
| Test Conditions | System of nominal capacity <ol style="list-style-type: none"> Before starting test, operate the system at constant electric power input corresponding to the nominal power level (e.g. 180 kW) and nominal temperature and pressure for 24 hrs (steady-state) Determine the average hydrogen production rate Followed by a change (10 min) to the upper power level (e.g. 300 kW) and operate at this power under steady-state for 24 hrs. Determine the average hydrogen production rate Followed by a change (10 min) to the lower operating power level (e.g. 9 kW) and operate at this power under steady-state for 24 hrs. Repeat step 1 and determine H₂ production rate |
| Number of Cycles | Set as required |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |

| METRIC | FREQUENCY | TARGET |
|---------------------------------|---------------------------------|--|
| Hydrogen production rate | BoT and EoT Step 3 Step 5 | > 80 kg H ₂ /day at 180 kW > 140 kg H ₂ /day at 300 kW > ~4 kg H ₂ /day at 9 kW |
| Energy consumption / Efficiency | BoT Following 1 cycle | <48 kWh/kg H ₂ or >82% vs. HHV at 80 kg H ₂ /day |
| Performance loss | After specific steps | Low decrease in hydrogen production rate (<0.007%/day) |

4.3.2 Start-up and ramp rates

The system is assessed to verify if it can reach the HPEM2GAS targets in terms of fast response. This is an important characteristic for grid-service since the system is expected to operate mainly when there is a surplus of renewable energy fed to the grid.

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

Validation of fast response (warm and cold start up)

System operation under stationary conditions

Protocol and Metrics

| | |
|----------------------------|--|
| System Conditioning | Operate the system at ~50% of nominal capacity and for sufficient time (4 hrs) to guarantee appropriate stack/sub-systems conditioning. |
| Test Conditions | System of nominal capacity <ol style="list-style-type: none"> 1. Before starting test, operate the system at constant electric power input of 180 kW and nominal temperature and pressure for 24 hrs (steady-state) 2. Proceed with complete Shut-down of the system for 24 hrs (Appendix B) 3. Start-up the system in a <i>step-change</i> from 0 to 180 kW input power 4. Reduce input power from 180 kW to 9 kW in a <i>step-change</i> and keep the system under steady state for 1 hr 5. Followed by a <i>step-change</i> to 180 kW and operate at this power under steady-state for 1 hr. 6. Followed by a <i>step-change</i> to 9 kW and operate at this power under steady-state for 1 hr. 7. Record variation of electrical properties and H₂ production rate vs. time during all steps and report. 8. Shut-down the system |
| Number of Cycles | Set as required |
| Temperature | Set as required, must be recorded and reported |
| Pressure | Set as required, must be recorded and reported |

| METRIC | FREQUENCY | TARGET |
|-----------------------------------|-----------|---|
| Rapid cold start capability. | | <2 min from 0 to 180 kW |
| Rapid ramp-up/ramp down operation | | <2 seconds from 5% to 100% load (from 9 to 180 kW); |

| | | |
|--|--------------------------|--|
| Hydrogen production rate | BoT and EoT | > 80 kg H ₂ /day at 180 kW > ~4 kg H ₂ /day at 9 kW |
| Energy consumption / Efficiency | BoT Following 1 cycle | <48 kWh/kg H ₂ or >82% vs. HHV at 80 kg H ₂ /day |
| Performance loss | After specific steps | Low decrease in hydrogen production rate (<0.007%/day) |

4.3.3 Duty cycles tests

The PEM electrolysis system is thereafter tested in the presence of duty cycles simulating grid service operation to test stability for coupling with grids sharing large fraction of intermittent renewable energy sources. The behaviour of grids sharing electrical power from wind turbines is studied by two Consortium partners (SWE, HS EL) in relation to local and distributed energy generation in Emden, Germany. From this analysis, a simplified testing protocol is derived.

System operation under duty cycles simulating grid service Protocol and Metrics

| | | |
|--|--|--|
| Test bench preparation | <ul style="list-style-type: none"> Determine the current profile from the specific electric grid under consideration sharing renewable energy sources on a time basis of 24 h for low, moderate and high power fluctuations. Transfer this profile to a function generator set-up of the power conditioning/controls unit of the electrolysis system | |
| System Conditioning | Operate the system at ~50% of nominal capacity and for sufficient time (4 hrs) to guarantee appropriate stack/sub-systems conditioning. | |
| Test Conditions | <p>System of nominal capacity</p> <ol style="list-style-type: none"> Before starting test, operate the system at constant electric power input of 180 kW and nominal temperature and pressure for 24 hrs (steady-state) Determine the average hydrogen production rate Followed by a duty cycle (24 hrs): <ul style="list-style-type: none"> Apply the low power fluctuation profile to the system At the end of the test, determine the average hydrogen production rate during 24 hrs (steady-state operation at 180 kW) Repeat steps 3 and 4 for the intermediate power fluctuation profile Repeat steps 3 and 4 for the high power fluctuation profile | |
| Number of Cycles | 4 (~ 1 month) | |
| Temperature | Set as required, must be recorded and reported | |
| Pressure | Set as required, must be recorded and reported | |
| METRIC | FREQUENCY | TARGET |
| Hydrogen production rate | BoT and EoT | >80 kg H ₂ /day at 180 kW |
| Energy consumption / Efficiency | BoT Following 4 cycles | <48 kWh/kg H ₂ or >82% vs. HHV at 80 kg H ₂ /day |

| | | |
|-------------------------|--|--|
| Performance loss | After specific steps Following 4 cycles | Low decrease in hydrogen production rate in line with steady-state tests (<0.007%/day) |
|-------------------------|--|--|

Determination of the current profiles associated to low, moderate and high power fluctuations will be carried out during the execution of the project. This will regard the electric grid located at the Emden City Council Municipality, Germany which is sharing a large amount of renewable energy sources. A detailed analysis will be reported in a next deliverable report D2.2- Complete set of technical and operational requirements for field-testing. The Emden City Council is the site selected for field tests.

4.3.4 Field tests

Field tests deal with the assessment of the advanced electrolyser in a real environment for grid-balancing. The PEM electrolysis system is thus assessed in field-tests by directly interfacing it with the Emden city council grid in Germany. The following protocols represent a first guideline for the PEM electrolyser field tests that can be implemented/modified during the execution of the project and updated procedures reported in the successive deliverables of this workpackage.

Protocols for Field testing the PEM electrolysis system in grid-balancing service Protocol and Metrics

| | |
|--|--|
| Water electrolysis system characteristics | BoP developed around a nominal capacity stack capable of providing a hydrogen production rate of 80 kg H ₂ /day nominal (up to 140 kg H ₂ /day transient) with 180 kW nominal (300 kW transient) power input. BoP equipped with proper AC/DC and DC/DC step-down converters depending on the specific characteristics of the grid. |
| Interfacing characteristics | Interfacing the PEM electrolysis system to the SWE water, gas and electricity grids at the Emden city council |
| Test Conditions | <ol style="list-style-type: none"> 1. Before starting the field test, operate the system at ~30% of nominal capacity for 24 hrs at steady-state through the power conditioning/control unit. 2. Increase power input to 180 kW and operate the system at 100% of nominal capacity for 24 hrs at steady-state through the power conditioning/control unit. 3. Determine hydrogen production capacity and hydrogen quality at the specific power consumption, temperature and pressure conditions. 4. Connect the electrolyser system directly to the grid for > 6 months 5. Monitor electrical profile characteristics from the grid, hydrogen production rate and hydrogen quality from the electrolyser. 6. Register system performance/efficiency in terms of hydrogen production capacity as function of the input profile from the grid. 7. At the end of the test, determine power consumption for the system at 100% of nominal capacity for 24 hrs at steady-state through the power conditioning/control unit as defined previously. |
| Temperature | Set as required, must be recorded and reported |

| | | |
|--|--|--|
| Pressure | Set as required, must be recorded and reported | |
| METRIC | FREQUENCY | TARGET |
| Hydrogen production rate | BoT and EoT | >80 kg H ₂ /day at 180 kW |
| Total hydrogen production | | Ability of >15 tons H ₂ (5N) production in grid balancing conditions. |
| Energy consumption / Efficiency | BoT and EoT | <48 kWh/kg H ₂ or >82% vs. HHV at 80 kg H ₂ /day |
| Performance loss | Following field test | Low decrease in hydrogen production rate in line with steady-state tests (<0.007%/day) |

The PEM electrolysis system is validated in Field Test > 6 months at Emden council, Germany. The electrical profile characteristics from the grid, the hydrogen production rate and hydrogen quality are monitored and reported **(MS7)**.

5 Aspects related to safety issues

Hydrogen is a highly flammable gas that has been associated with several high profile disasters. 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 that need to be considered when developing a PEM electrolyser is given below. This is in no way all encompassing but is rather intended as an introduction. Further information should be sought from such references as the British Standard BS ISO 22734-1, <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 embrittle 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 reaction between hydrogen and/or oxygen with all materials used in the construction of the electrolyser must be very slow. In addition, 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% volume fraction of hydrogen in air within the hydrogen generator. 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 Implementation of the EU harmonised test protocols for water electrolysis application in HPEM2GAS

As discussed in the introduction, a parallel set of protocols is derived from the draft of the document on electrolysis testing produced by JRC (EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS). This was prepared with the active contribution of several FCH JU program actors including the HPEM2GAS partners and other important international stakeholders. At this time of preparation of the present deliverable, the JRC document is still not in the final form. Thus, an eventual update of this section can be provided as Appendix in the next deliverable of this workpackage i.e. D2.2 Complete set of technical and operational requirements for field-testing.

Regarding the harmonisation of the protocols and testing procedures, we have essentially referred to the EU HARMONISED TEST PROTOCOLS led by JRC, but at the same time we have not excluded similar reports produced in parallel by other organisations such as the International Energy Agency. These were acquired as well and, in part, adopted in the internal set of protocols. However, in order to produce a concise analysis, in this section, we have treated specifically the set of EU harmonised protocols. This document should be widely adopted within the FCH JU program (FCH JU projects). Thus, assessing the PEM electrolysis devices according to these procedures will provide anyway a useful basis for comparison within the FCH JU program. This is in line with the objective of harmonisation of HPEM2GAS.

The document prepared by JRC is aiming at harmonising a set of protocols and testing procedures valid for assessing electrolysis devices with respect to the Key performance indicators (KPIs) defined in the Multi-Annual-Work Plan of the FCH JU. This document is produced with the contribution of a significant number of stakeholders, and includes different requirements of the various FCH JU programs in this field. These are essentially general protocols which are extremely useful to provide a fair comparison of the results and achievements within the different organisations and programs. However, for the present case, it was necessary to adapt and implement such protocols according to the specifications of the HPEM2GAS project. As an example, in HPEM2GAS, the efficiency and performance targets in single cell are defined at very high current densities i.e. 3 and 4.5 A cm⁻². Thus, this required to extend the data acquisition for the polarisation curves defined in the EU harmonised set of protocols to higher current ranges.

In the following, the set EU harmonised protocols used in HPEM2GAS is discussed, implemented and compared to the HPEM2GAS internal protocols. The topics addressed in the EU harmonised set of protocols are essentially dealing single cells (MEAs) and short stacks. Thus, the analysis is here restricted to these aspects.

6.1 Key-Performance Indicators

Key-performance indicators regard performance, efficiency, stability, dynamic behaviour. It is important to define these parameters in the same way to favour comparison of the results achieved in different projects.

6.1.1 Performance

In the *EU harmonised set of protocols*, the performance of the water electrolysis process is assessed from polarization curve measurements in the galvanostatic mode (constant current density). Additional tests regard

ac-impedance measurements and hydrogen crossover. The approach for all these tests is essentially the same approach discussed in HPEM2GAS internal protocols. Polarisation curves are recorded in both modes (increasing and decreasing currents) in the EU protocols to check for hysteresis.

Hysteresis issues are reduced in the HPEM2GAS internal protocols by keeping as much as possible constant the temperature during the polarisation experiments by using thermostated water recirculation.

In the *EU harmonised set of protocols*, Performance Criteria for both Reference Operating Conditions and Stressor Conditions are:

- cell voltage at 1.0 A/cm² ; cell voltage at 2.0 A/cm² ; cell voltage at 3.0 A/cm²

whereas in the *HPEM2GAS internal protocols*, performance is assessed as:

- cell voltage at 3.0 A/cm² ; cell voltage at 4.5 A/cm²

The latter are in line with the specific project milestones. However, there is at least one current density value for comparison.

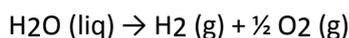
6.1.2 Efficiency

➤ Energy consumption:

In the *EU harmonised set of protocols*, the energy consumption of the water electrolysis process per unit of H₂ mass is expressed in kWh/kg H₂. This is in line with the definition given in the *HPEM2GAS internal protocols*. At the system level, it is taken into consideration the energy consumption of all ancillary equipment used in the electrolysis system.

➤ Energy efficiency:

Since water is fed in liquid form to the electrolysis device (no steam feed), HHV values are used to determine efficiency for:



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

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

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

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

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

These definitions are essentially equivalent in the *EU harmonised set of protocols* and in the *HPEM2GAS internal protocols*.

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

Thus, the voltage efficiency should be multiplied by the current efficiency to get the actual total efficiency of the cell as defined in HPEM2GAS internal protocols. This is also agreed in the harmonised EU protocols. Thus:

$$\epsilon = \epsilon_V \cdot \epsilon_i$$

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

$$\eta_{cell / stack}^{HHV} = \frac{HHV}{P_{cell / stack}} \cdot \dot{n}_{H_2} \cdot 100 \%. \quad \eta_{system}^{HHV} = \frac{HHV}{P_{extern}} \cdot \dot{n}_{H_2} \cdot 100 \%.$$

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

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

These definitions are in line with those given in HPEM2GAS internal protocols.

6.1.3 Stability

➤ Average voltage degradation

The *EU harmonised set of protocols* draft reports: Average cell voltage degradation is the voltage increase per hour recorded during the test of 1000 hrs at fixed current of 1 A cm^{-2} excluding the first 100 hrs of conditioning and considering only the time range where the cell potential continuously increases with time.

This is essentially similar to that of the *HPEM2GAS internal protocols* that however consider best line fit.

The definition given in the *EU harmonised set of protocols* tries to avoid that the degradation rate is affected by artefacts caused by a negative cell voltage trend due to cell conditioning after a start procedure. Regarding the stability assessment, the *EU harmonised set of protocols* also distinguishes between reversible and irreversible degradation.

The determination of the **reversible degradation** during durability tests including start-up / shut-down cycles is determined in the EU protocols according to a specific method.

The **reversible voltage loss** $\Delta V_{rev,i}$ can be calculated as the difference between the cell voltage $V(t_{i+1})$ at the starting time t_{i+1} of the test block $i+1$ and the voltage $V(t_i + \Delta t_i)$ at the ending time $t_i + \Delta t_i$ of the test block i as follows:

$$\Delta V_{rev,i} = V(t_{i+1}) - V(t_i + \Delta t_i).$$

Δt_i is the time between a start-up and a shut-down.

The **irreversible (non-recoverable) part of the voltage loss** due to a test block i is determined from the variation between the cell voltage $V(t_i)$ at starting time t_i of the test block i and the voltage $V(t_{i+1})$ at the ending time t_{i+1} of the recovery period $\Delta t_{r,i}$ (i.e. the voltage at starting time t_{i+1} of test block $i+1$) as follows:

$$\Delta V_{irrev,i} = V(t_{i+1}) - V(t_i).$$

Both approaches will be investigated in HPEM2GAS and the stability characteristics compared according to the two different data treatments.

The experimental procedure is the same in both protocols.

6.2 Harmonised Reference Operating Conditions

The EU Harmonised Reference Operating Conditions for PEM water Electrolysis for Single Cell and Stack Testing are reported in the following table. **These are also used in HPEM2GAS to harmonise operating characteristics for reference conditions.**

| | Parameters | Symbol | Unit | Reference Settings ® |
|---------|---|---------|--------------------------------------|-------------------------|
| | Nominal cell operating temperature | T.Si.CL | °C | 80 |
| ANODE | water inlet temperature | T.Si.A | °C | 80 |
| | water inlet pressure (absolute) | p.Si.A | kPa | 100 |
| | Water quality | | MOhm.cm | >5 (ISO 3696 scale 2) |
| | Water inlet flowrate (with recirculation) | F.Si.A | g min ⁻¹ cm ⁻² | 1 |
| CATHODE | Oxygen outlet pressure | p.So.C | kPa | 100 |
| | Hydrogen outlet pressure | p.So.C | kPa | 100 |
| | Hydrogen Quality | | | 5N |

6.3 Stressor tests effects

Deviations from the standard operating conditions may result in degradation of performance and durability. Both higher and lower variations from the reference operating conditions are considered as Stressors.

Low and High Values of Stressor Conditions set in the *EU harmonised set of protocols* are reported in the following table. **These are also used in HPEM2GAS to harmonise operating characteristics for testing PEM electrolysis devices with respect to harsh operating conditions.**

| | Parameters | Symbol | Unit | Low Settings (L) | Reference Settings ® | High Settings (H) |
|---------|------------------------------------|---------|--------------------------------------|---|----------------------|-------------------|
| | Nominal cell operating temperature | T.Si.CL | °C | 30 | 80 | 140 |
| ANODE | water inlet temperature | T.Si.A | °C | 30 | 80 | 90 |
| | water inlet pressure (absolute) | p.Si.A | kPa | 100 | 100 | 300 |
| | Water quality | | MOhm.cm | >5 (ISO 3696 scale 2); <1 for water quality stressor | | |
| | Water inlet flowrate (with | F.Si.A | g min ⁻¹ cm ⁻² | 0.5 | 1 | 1.5 |
| CATHODE | Hydrogen outlet pressure | p.So.C | kPa | 30 | 100 | 3000 |

Normalised performance is determined as follows:

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

This approach is also adopted in HPEM2GAS.

Normalised performance output equal to zero means no degradation. When the stressor causes performance degradation, $V_{\text{stressor}} > V_{\text{reference}}$, their ratio is > 1 and the normalized performance output is negative. If the stressor increases the performance (e.g. the temperature), the normalized

performance output is positive. However, an eventual positive effect of the stressor on performance may instead be negative on durability.

6.4 Load cycles

The *EU harmonised set of protocols* considers dynamic tests in terms of load cycles simulating real life electrolysis applications namely for:

- STATIONARY
- INTERMITTENT RENEWABLE POWER SUPPLY
- GRID BALANCING

and accelerated stress tests.

Further tests deal with cold start, start up - shut down etc.

The general strategy is similar to the internal protocols of HPEM₂GAS. In the *EU harmonised set of protocols*, cycle tests consist in rapid on-off cycles between 0 and 100% load at ambient pressure. Variable cycling test (dynamic current cycling tests) are essentially represented by steps of current of 60 s between 0%, 50% and 100%.

This approach is not adopted in HPEM₂GAS because the dynamic behaviour that needs to be assessed in this project regards specific targets, e.g. the specific operation capacity range (5%, 100% and 160 %) and the fast response target of the device e.g. 2 s for warm start up that requires to operate the system in a step-change.

7 Conclusions

The protocols and procedures defined in this deliverable are intended as means of verification to assess the achievements of the project milestones, in particular the targeted hydrogen production rate and efficiency in the specific range of operating temperature and pressure. These include an assessment of the capability of the PEM electrolysis system to operate in grid-balancing service for grids sharing large amount of renewable power sources.

The procedures reported here comprise validation of optimised and scaled-up active components, MEAs, stack and PEM electrolysis systems. In general, these procedures will provide a systematic approach to test materials, components, and systems in order to validate them for PEM electrolysis application with particular regard to grid-service.

The aim is to assess components and sub-system device by specific testing procedures in order to deconvolute the properties of each system component. This can allow identification of specific interface drawbacks between the various system sub-components and can address the materials development towards the best combination of membrane, electrocatalysts, assembling procedures, stack housing, system BoP for the specific application.

The aim is also to compare system performance with stack and single cell performance at specific current densities and to determine energy consumption at the nominal production capacity.

Moreover, the objective is to determine a set of protocols for assessing performance degradation in terms of terminal voltage increase in steady-state tests and duty cycle experiments.

These protocols are necessarily developed to assess the specific HPEM2GAS project objectives and milestones; however, the aim is also to propose harmonized testing for PEM electrolysis components and systems establishing agreed and shared operation procedures among different partners involved in this project and to provide a basis for comparison to research performing entities outside HPEM2GAS.

The obtained data will be presented in table form as reported in the Appendix.

8 Appendix A – Tables of characterisation data

Tables of characterisation data

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 ₂ O at specific T °C | wt % | | |
| Thickness increase Δz in H ₂ O at specific T °C | % | | |
| MD increase Δx in H ₂ O at specific T °C | % | | |
| TD increase Δy in H ₂ O at specific T °C | % | | |
| Through plane conductivity in H ₂ O at specific T °C | mS cm ⁻¹ | | |
| Area resistance in H ₂ O at specific T °C | Ω cm ² | | |
| In plane conductivity in H ₂ O 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 mC cm ⁻² | | |
| OER overpotential (IR-free) at 3 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 3 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 3 A cm ⁻² and 3 A cm ⁻² at specific temperature (°C) and pressure (bar) conditions | V | | |

| | | | |
|---|----------------------------|--|--|
| Performance degradation (cell increase) in steady-state tests at 1 A cm ⁻² and 3 A cm ⁻² at specific temperature (°C) and pressure (bar) conditions | μV/h | | |
| Performance degradation in accelerated tests at specific temperature (°C) and pressure (bar) conditions | % loss | | |
| H ₂ Crossover equivalent current density and % of H ₂ in O ₂ | mA cm ⁻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 3 A cm ⁻² and 4.5 A cm ⁻² at specific temperature (°C) and pressure (bar) conditions | V V/cell | | |

| | | | |
|---|---|--|--|
| Performance degradation (stack voltage increase normalised per cell) in steady-state tests at 3 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 3 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 rump up (from 5% to 100%) | s | | |
| Performance loss in duty cycles | % decrease hydrogen production rate /day | | |
| Total hydrogen production in field tests | tons H ₂ | | |
| Hydrogen production in field tests referred to the energy input | kg H ₂ /kWh | | |
| Performance loss in field tests | % decrease hydrogen production rate /day | | |

9 Appendix B – Reference shut-down procedure for PEM electrolysis devices

Pressure should be decreased to ambient conditions (gas vented to the atmosphere) while the device is operated at the nominal current density, there after the current is decreased in steps (20% of the nominal current) every 10 min and the auxiliaries are put off when the system is in OCV, cathode compartment is vented with nitrogen.