



Enhanced performance and cost-effective materials for long-term operation of PEM water electrolyzers coupled to renewable power sources

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DELIVERABLE REPORT

D.2.1 – PROTOCOLS FOR CHARACTERISATION OF ACTIVE COMPONENTS

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NATURE OF THE DELIVERABLE

R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY	
Keywords	<i>Membranes, Catalysts, MEAs, Characterisation, Procedures, Protocols</i>
Abstract	<p>The objective of this deliverable is to define characterisation and test protocols for the assessment of performance, efficiency and durability of the newly developed PEM electrolyser components.</p> <p>The procedures and methods defined within are a set of protocols for <i>ex-situ</i> and <i>in-situ</i> characterisation of active components such as membranes, catalysts, and electrode-membrane assemblies (MEAs). Included are steady-state and accelerated durability tests as well as performance evaluation under specific operating conditions.</p> <p>Baseline components against which progress is assessed, in terms of durability and performance cost, are identified.</p>

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D.2.1 – PROTOCOLS FOR CHARACTERISATION OF ACTIVE COMPONENTS

1. INTRODUCTION

This deliverable is concerned with:

- The establishment of a set of characterisation and testing protocols for *ex-situ* and *in-situ* characterisation of PEM electrolyser membrane, electro-catalysts and MEAs. These procedures include steady-state and accelerated durability tests, as well as performance evaluation in relation to the specific operating conditions and applications.
- Establishment of a benchmark of baseline components against which progress may be assessed in terms of durability and performance.

The testing protocols, parameters and procedures for the assessment of active components are defined, to allow for a homogeneous screening and evaluation of the newly developed components. Appropriate testing protocols are necessary to individually screen materials to find those that provide the best performance. Measurement protocols are defined for both *ex-situ* physico-chemical and electrochemical characterisation, and will be used to validate the quantitative project targets in terms of performance and durability.

For membrane assessment, the procedures include; in-plane and/or through plane conductivity measurements as a function of temperature and R.H. (for high temperature operation). *Ex-situ* ageing protocols such as the Fenton reactions in the liquid phase, hydrolytic stability, equivalent weight, gas permeability, water uptake and dimensional change, differential scanning calorimetry and mechanical properties by tensile strength measurements.

For the electrocatalyst assessment, the procedures include; specification of catalyst loading in the electrodes, catalyst properties, methodologies for the determination of particle size and catalyst dispersion and *ex-situ* characterization and screening of the catalysts in half-cell electrochemical tests. Definition of measurement protocols for cyclic voltammetry with determination of voltammetric charges, polarisation curves and AC-impedance spectroscopy measurements. Specific protocols and apparatus for steady-state galvanostatic polarization measurements have been defined to determine mass activity and performance at specific potentials in relevant ionomer systems, temperature and pressure conditions. Identification of electrochemical characterisation protocols for the determination of electrocatalytic parameters such as electrochemical active surface area, Tafel slopes, charge transfer resistance, etc. Identification of accelerated stress test protocols such as potential cycling, prolonged operation at high potentials, supported by *ex situ* post-test analysis, to evaluate the degradation of both catalyst active phase and support.

For the MEA assessment, the procedures include; the determination of performance, efficiency (both electric and faradaic), identification of conditions relevant to the applications, durability under steady-state testing conditions, accelerated procedures, as well as normal and prolonged operation and MEA ageing under practical operation.

These protocols regard polarization curves, cross-over measurements as function of temperature, pressure and current density. Protocols for lifetime and stability testing are selected and include post-testing *ex-situ* physico-chemical characterization.

Further specification concern with provision of electro-catalyst and membranes for MEAs testing.

These procedures are used as means of verification to assess the achievement of project milestones.

2. PROTOCOLS

2.1. Membrane assessment:

Three sets of testing procedures for the characterisation protocols have been identified. The first set of procedures will be used to select the membranes for further evaluation based on the minimum required properties, whereas a second set of procedures include a wider range of characterisation protocols that are to be used for the most promising membranes. A third set of procedures include specific assessment under critical conditions relevant to PEM electrolysis applications.

Description of these methods are reported below. As more than one method can be used for the determination of a specific parameter, the method that is adopted will be reported in a data-set table identifying membrane characteristics.

Pre-treatment of the membrane before measurements is herewith identified:

The membranes should be acidified before characterisation according to the following prescription:

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

2.1.1 First set of testing procedures - General aspects

The priority list provides general aspects for membrane evaluation such as solubility, swelling and handling as a minimum required properties of membranes for further evaluation.

- solubility and stability test in water at the boiling temperature (100 °C): sample must not dissolve or swell excessively (< 30 %).
- no leach-out of functional groups as determined by IEC measurement (< 1%). Refer to appendix 5.2 for measurement procedure.

- handling in dry and wet state as well as after the treatment in boiling water: sample must not break when bent.

2.1.2 Second set - Characterisation under standard conditions

The second set of procedures provides characterisation protocols under standard conditions with respect to the following membrane properties:

-Polymer type including reinforcement material.

-Ion exchange capacity: protonic membrane processing with 0.1 M NaCl at RT for 12 hrs followed by titration with 0.1 M NaOH. Alternatively: equilibration in 0.01M KHCO₃, room temperature, minimum 16 hrs. 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 (dry/humidified/hydrated states)

Thickness measured across the membrane using a micrometer screw gauge.

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

-Conductivity assessment in a wide range of temperatures (R.T. to 120 or 150 °C, in steps of 10 °C), pressure (ambient pressure, 3 bar, 5 bar with further steps of 5 bar) and R.H. conditions (in steps of 25% RH). Methods: in-plane or through plane / 4-electrode set-up, AC impedance, high frequency intercept.

The membrane is placed in a conductivity cell and allowed to equilibrate at the desired temperature and relative humidity. Measurements are also carried in the presence of H₂ and O₂ gases at various pressures and differential pressures.

-Uptake of water: A rigorous procedure is indicated in section 5.7. For pre-screening, a simple approach is here reported: equilibration for 1 h under specific conditions, 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.

-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. See also section 5.7.

Alternatively: 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.

Each sample submerged in fixed volume of water in sealed container at constant temperature for required length of time.

Water removed from surface prior to mass measurement using lint-free and non-wicking material

Samples then dried to constant mass in desiccator

% Linear Expansion Coefficient (LEC) is defined by:

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

% Water Uptake (WU) is defined by:

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

% Water Content (WC) is defined by:

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

-H₂ and O₂ permeability measured by using specific sensors; alternatively, H₂ permeation it may be also determined *in-situ* under differential pressure using the conventional electrochemical methods (see MEA section).

- 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).

Properties such as thermal stability at a given temperature, Glass transition temperature, melting point, thermal decomposition and curing temperature may not be necessarily reported in the membrane data-set.

2.1.3 Third set - Characterisation under project relevant conditions

-Membrane characterization under differential pressure: an 8 cm² Differential Pressure Cell will be used This cell can be pressured hydrostatically to 30bar or pneumatically up to 100bar if appropriate.

The tests will assess burst pressure under various conditions and generally how the membrane and/or an MEA responds to pressure.

- Through plane conductivity with and without catalyst: this approach will be used also to measure contact resistances (diffusion media-catalyst; catalyst-membrane; diffusion media-current collector). Measurements are performed under water.
- Oxidative Stability: Fenton's Reagent Test - 3% H₂O₂, 4 ppm Fe²⁺ ions at 60 °C for 4 h. Measure mass loss.
- Hydrolytic Stability: Hot Water Solubility Test – Pure water, at 95 °C for 24 h. Measure mass loss Membranes is initially conditioned then dried prior to testing. Membranes washed thoroughly with water and mass loss determined after drying. Membranes are also to be tested for mechanical integrity and change in IEC after soak test has been carried out.
- Tensile testing and tear resistance measured according to the following:

ASTM D882 - 10 Standard Test Method for Tensile Properties of Thin Plastic Sheeting

ASTM D638 - 10 Standard Test Method for Tensile Properties of Plastics

ASTM D1004 - 09 Standard Test Method for Tear Resistance (Graves Tear) of Plastic Film and Sheeting

ASTM D1922 - 09 Standard Test Method for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method

Other mechanical properties that can be tested are;

Shear – ASTM D732 - 10 Standard Test Method for Shear Strength of Plastics by Punch Tool

Compression

Creep

2.1.4 Baseline (benchmark) membrane

The baseline (benchmark) membrane will be Nafion 115 (DuPont).

2.1.5 Data-set

Depending on its characteristics, each membrane can be subjected to either one, two or all three sets of characterization. The data reported in a specific data-set table should represent a finger-print of the main properties of the membrane and will serve to build up relationships between performance in cell and main features of the polymer electrolyte. An example of the data-set table is reported at the end of this document as guideline for reporting specific membrane properties.

3. 1. Electrocatalysts assessment:

Electrocatalyst assessment is to be carried out in half cell and single cell. In the latter case, an MEA configuration is used. Accordingly, protocols for electrocatalyst assessment in single cell and for MEA characterization are essentially the same and will be treated in the same section. From these experiments and relative data treatment, information related to the electrocatalyst performance and durability will be deconvoluted from MEA evaluation.

3.1.1 Catalyst's support assessment:

Experiments, serving as a screening tool to compare the electrochemical degradation in an acidic environment of different oxide supports, are defined here. For these experiments, the selected electrolyte is 0.5 M sulfuric acid or well as 0.1 M HClO₄ and the temperature is 75-80 °C. Electrochemical corrosion specifically involves the oxygen evolution catalyst/support.

The liquid electrolyte will provide a proper environment in terms of water content and proton activity and these experiments will be useful to predict the level of corrosion in the PEM water electrolyser.

The procedure consists of applying 1.4 V RHE for 2 h to the support under investigation. The support is mixed with a standard Nafion ionomer (67% support-33 % wt. Nafion) and deposited on a Ti-grid. For formulations based on sub-stoichiometric or doped Ti/Sn oxides, an oxidation charge is recorded in a wide potential window and it is associated with double layer discharging, surface reactions involving adsorbed intermediates. At a potential of 1.4 V RHE, no oxygen evolution occurs (the thermoneutral potential is 1.48 V RHE) but oxidation of sub-stoichiometric species (e.g. from Ti³⁺ to Ti⁴⁺) within the support which may cause erosion and dissolution may occur. As an example, the presence of Ti³⁺ species is essential to provide proper electronic conductivity. Formation of Ti³⁺ is promoted by doping with Ta⁵⁺, Nb⁵⁺ species to maintain the electro-neutrality within the crystallographic structure or it is induced by high temperature reduction in sub-oxides e.g. Ebonex type (Magneli phase). In this regard, it is appropriate to evaluate the electrochemical stability as inversely related to the oxidation charge and it is important to normalize this parameter by sample weight and possibly by BET surface area. The support degradation is thus estimated from the integrated oxidation/corrosion current in a 2 h potential holding test at 1.4 V RHE.

In addition, the support can be subjected to a steady-state operation at 2.2 V for 2 h and reference cyclic voltammetry analysis (see below) is carried out at regular intervals to investigate surface area modifications.

Ex-situ physico-chemical analysis pre- and post-operation by XRD, XPS, TEM, SEM-EDX and XRF is to be carried out to elucidate structural, chemical, surface and morphology changes in the support.

3.1.2. Electro-catalyst evaluation:

Screening of catalysts is carried out at both half cell and single cell level in the presence of reference electrolytes and polymer membranes developed in the project. The tests in single cell, specifically dealing with catalyst characterization, are carried out in the conventional or driven-mode using a proper floating reference electrode. Such methods will allow testing of the electro-catalyst in the presence of a variety of polymer electrolytes to get information about the interfacial properties.

The proposed reference electrolytes are sulphuric acid for operation in a liquid electrolyte half cell and Nafion 115 in combination with Nafion inomer in the electrodes (initial formulation 67% catalyst and 33% ionomer content in the catalytic layer) for single cell. The amount of ionomer in the catalytic layer results, from previous studies, as a good 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.

3.1.2.1 Electrocatalyst testing in half cell:

- Half cell investigation is carried out with regard to both anode and cathode reactions to individuate activation overpotentials, stability in acidic environment and electrocatalytic activity. The reference temperature for half cell testing will be 75°C. The reference electrode is Hg/HgSO₄ Mercury-mercurous sulfate Electrode (MSE) (0.65 V vs RHE) in sulphuric acid or Hg/Hg₂Cl₂ Saturated Calomel Electrode (SCE) (0.24 V RHE) in perchloric acid.

The baseline anodes consist of a GDL type Ti-layer and a catalytic layer containing 2-3 mg cm⁻² of PGM (Ir and/or Ru) loading with 33% wt. ionomer. The baseline cathodes are based on a standard 40% Pt/Vulcan catalyst at 0.5 mg cm⁻² with carbon paper/cloth gas diffusion backing layer.

Pre-screening is carried out in liquid electrolyte by half-cell galvanostatic polarization measurements for hydrogen and oxygen evolution in 0.5 M H₂SO₄ /0.1 M HClO₄ by using electrodes similar to those developed for single cell testing. For the oxygen evolution, a sample holder based on a Ti grid backing is used.

Protocols for anode and cathode polarization curves are herewith reported: change the anodic or cathodic current density and record the corresponding variation of preferably in steps as 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	

Current Density [A·cm ⁻²]	Cell Voltage [V]
0.45	
0.5	
0.6	
0.7	
0.8	
0.9	
1	
1.1	
1.2	
1.3	
1.4	
1.5	
1.6	
1.7	
1.8	
1.9	
2	

The cut-off voltage is fixed at 2.0 V RHE for the anode and -0.5 V RHE for the cathode. Measurement data logging will occur at a frequency of 1-0.1 Hz, the potential at a given current density is to be averaged over the last 1 min of the measurements and plotted against the current density. At the end of the I-V curve measurements, the current density will be set to zero (OCV).

AC-impedance is carried out in potentiostatic mode or under galvanostatic mode according to the procedure described below in the MEA section. Overpotentials are determined from IR-free Tafel plots. Ohmic resistance is determined from series resistance in the AC-impedance spectra.

Reference cyclic voltammetry will be carried out in the potential range 0-1.2 V RHE for the cathode and 0-1.4 V RHE for the anode with a sweep rate in the range 20-150 mV s⁻¹. Determination of ECSA for the 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; whereas for the anode, active area expressed as specific charge q* is obtained from integration in the entire potential window.

The double layer capacitance is related to the active surface area and is reported as mF cm⁻² and/or mF mg⁻¹. The capacitance in mC/cm² is calculated from AC-impedance, preferably at OCP, and it is divided by the catalyst loading in mg. Deconvolution of the double layer capacitance from the pseudo capacitance can be done using equivalent circuits, this method serves mainly as comparison. A second approach is to carry out Cyclic Voltammetry at room temperature at 20 mV s⁻¹ in the range 0-1.4 V where no faradaic reactions occur regarding water splitting. Water is supplied to the anode (nitrogen saturated). Adsorption processes are measured in the overall potential range and the voltammetric surface charge is determined by

integration. 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. Thus, we do not have a term of comparison, such as in the case of H-adsorption on Pt (0.210 mC/cm^2). However, we can use this approach to compare different catalysts/electrolyte interfaces for the anode electrochemically active surface area and the results achieved in different laboratories.

Anode catalyst degradation in half-cell is investigated by accelerated tests consisting of potential holding at 2.2 V for 48 h as well as by using potentiodynamic cycling between 1.4 and 2.2 V RHE (sweep rate 150 mV s^{-1}) in 10^4 cycles. Potential holding at -0.2 V vs. RHE for 48 h will be used to test the stability of the cathode in a three-electrode configuration mode. Reference cyclic voltammetry to investigate ECSA loss will be carried out at defined intervals (every 8 hrs or after specific 10^3 , $5 \cdot 10^3$, 10^4 cycles). Pre- and post-operation physico-chemical analyses will be carried out by XRD (structural), XRF (elemental), TEM and SEM-EDX (morphological), XPS (surface analysis).

3.1.2.2 Electrocatalyst testing in single cell:

Electrocatalyst testing in single cell is essentially carried out using the same procedures reported above for the half cell characterization.

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 of anode catalysts (rate determining step), the cathode will act both as reference and counter electrode. In this specific case, for diagnostic purposes, the Pt loading at the cathode can be significantly larger (2 mg cm^{-2}) than the project target to avoid significant polarization of this electrode as required for a reference. Correction for ohmic drop, mainly due to the membrane, will allow to determine overpotentials at a specific current.

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 polarization.

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.

4. 1. MEA testing and electrocatalyst/membrane assessment in single cell

- It is the aim of the Consortium to use the same cell for catalyst, electrode and MEA screening in single cell. This will be an 8 cm^2 active area cell and will be designed and provided by ITM (MEA WP leader) under special agreement and according to the regulations identified in the Consortium Agreement. This will allow the testing of the materials that have passed the pre-screening in the same hardware in the various laboratories. However, for a rapid identification of the most promising materials in the pre-screening phase,

single cell hardware already available in the partners laboratories e.g. 5 cm², 25 cm² etc. will be used. Scale-up studies will concern sizes ≥ 100 cm².

- MEAs will be formed by proper methodologies to be developed in the Consortium Laboratories and provided to the partners for cross-comparison.

The selected reference membrane is Nafion 115 and to overcome dehydration effects at high temperature, the cell will be pressurized.

- Electrocatalyst screening in single cell will be carried out in a wide range of temperature (from RT to 120-150 °C) and pressure. Measurements at high temperature are to be carried out in the pressurised mode.

MEA testing is intended as a tool to investigate *in-situ* catalysts, membranes and their assembly. Two sets of procedures are herewith reported. One refers to standard MEA characterization whereas a second one is more specific to the targets and conditions of this project.

4.1.1 MEA characterization under standard conditions

4.1.1.1 Membrane: *In-situ* characterization dealing specifically with the membrane properties 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*. Protocols for *in-situ* cross-over measurements of gases under practical operation include sensor methods and electrochemical methods (H₂).

4.1.1.2 Electrocatalyst: catalyst testing in a single cell will be carried out to evaluate the electrochemical behaviour, preferably in a wide range of temperatures (R.T. to 120 or 150 °C, in steps of 10-20°C) and pressures (ambient pressure, 3 bar, 5 bar and further steps of 5 bar). A comparison between the electrochemical behaviour at high temperature and at 80 °C will be carried out to analyze the catalyst properties in relation to warm-up characteristics of the practical device.

The MEA testing procedure is herewith reported:

4.1.1.2 1. Cell conditioning step: the single cell must be equilibrated at 80 °C with de-aerated distilled water fed to both compartments at ambient pressure, pre-heated to this same temperature at a flow rate of 5 ml min⁻¹ for an 8 cm² cell.

Conditioning under an applied load of 0.2 A cm⁻² for 24 hours to favour membrane hydration and *in-situ* purification. This is only a guideline, and it can be adapted to reach the maximum power performance while keeping good system efficiency.

4.1.1.2.2. Polarization curves (cell voltage vs. current density or I-V): the main objective of the polarisation curve is to determine the change in the cell voltage for 1 min generated by variation of the current density preferably in steps as reported below:

Current Density [A·cm ⁻²]	Cell Voltage [V]	Current Density [A·cm ⁻²]	Cell Voltage [V]
0.0005		0.45	
0.001		0.5	
0.002		0.6	
0.005		0.7	
0.01		0.8	
0.02		0.9	
0.03		1	
0.04		1.1	
0.06		1.2	
0.08		1.3	
0.1		1.4	
0.15		1.5	
0.2		1.6	
0.25		1.7	
0.3		1.8	
0.35		1.9	
0.4		2	

For a cell test at a fixed cell temperature, inlet temperature must be maintained at the same cell temperature.

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 1-0.1 Hz. The cell voltage (and power density) at a given (averaged) current density is averaged over the last 1 min of the measurements and plotted against the current density. At the end of the I-V curve measurements, the current density will be set to zero (OCV) before stopping all the testing equipment.

Criteria for determining I-V curves:

-Influence of the cell temperature: by maintaining constant feed of the reactant as above, repeat the I-V curve measurements at increasing temperatures from RT or 40° to 90 °C (in steps of 10-20 °C). 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 to 150 °C under pressurised mode (in steps of 10-20 °C). Increase the pressure to 3 bar abs, 5 bar abs and further steps of 5 bar.

Two modalities will 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).

4.1.1.2 3. 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 and finally at the maximum achieved potential or under galvanostatic mode at 100 mA cm⁻² and 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.

4.1.1.2 4. Cross-over measurements are carried out *in-situ* under relevant temperature and pressure conditions by using the sensor method or electrochemical methods if applicable.

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

Assemble cell with potentiostat to control voltage and measure current

Specifically for cross-over measurements, flow 100% humidified hydrogen on Ir-Ru electrode (equiv. of 1.5 stoich at 1A/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 400mV against counter-reference electrode at 2mV/s – current limited by crossover rate from anode to cathode.

Crossover rate reported at 400 mV (1mA/cm² ≈ 0.070 ml/min/cm² hydrogen) under steady state.

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

4.1.1.2 5. Durability studies: steady-state galvanostatic operation at 0.5-1 A cm⁻² for at least 200 hrs under temperature and pressure relevant conditions identified during the execution of the program. 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 and TEM.

4.1.1.2 6. Electrochemical diagnostics for *in-situ* ECSA determination:

Reference cyclic voltammetry for the anode is carried out as specified for the half cell measurement by feeding humidified H₂ at the cathode (flow rate 100 ml min⁻¹). The dew-point temperature is equal to cell temperature. Reference cyclic voltammetry for the cathode is carried out as specified for the half cell measurement by feeding humidified H₂ at the anode (flow rate 100 ml min⁻¹). The dew-point temperature

is equal to cell temperature. The Pt/H₂ interface acts both as reference (RHE) and counter electrode. Determination of the ECSA is reported above for the half cell. This procedure can be in a first attempt adopted also with non-noble metal anode catalysts. Preferably, non noble metal catalysts should be tested in half-cell with an external reference electrode. For anode characterization, since the oxygen evolution is the rate determining step, we assume that the anode contribution is prevailing but the double layer capacitance contribution is lowered due to the contribution of both electrodes. Thus, the surface area determination from the capacitance values should be preferably carried out in half cell.

4.1.1.2 7. Accelerated stress tests:

Specific accelerated stress tests will be a high potential hold test i.e. 100 hrs potential hold at 2.2 V at relevant temperature and pressure operation conditions. Water feed, temperature and pressure as above.

4.1.1.2 8. Data treatment:

Electrocatalyst performance evaluation:

-anode overpotential (E_a) measured at 1 A cm⁻² under relevant temperature and pressure conditions from IR-free Tafel plots in the presence of high metal loading (> 2-3 mg Pt cm⁻²) cathode counter-electrode.

-cathode overpotential (E_c) measured at 1 A cm⁻² from the IR-free cathode polarization curve. This is determined as the difference E_c=E_{cell} –E_a where E_a is determined as above.

Ohmic resistance is determined from high frequency intercept on the real axis of the Nyquist plot obtained from AC-impedance spectroscopy.

MEA performance evaluation:

-cell potential is determined at 1-2 A cm⁻² under relevant temperature and pressure conditions. Voltage efficiency is determined as a function of thermoneutral potential, faradaic efficiency evaluated from cross-over data.

MEA durability:

Cell voltage decay determined by curve fitting in the entire time window of the steady state test at 1 A cm⁻².

5. APPENDIX – DETAILED SPECIFICATIONS AND PROCEDURES

5.0 ElectroHyPEM Membrane Specifications and Procedures

Summary of Procedures

Procedures

Number	Test
1	In-Plane Conductivity and/or through plane
2	Measurement of Membrane Ion Exchange Capacity and Equivalent Weight
3	Membrane Chemical Stability – Fenton’s Test
4	Membrane Hydrolytic Stability Test
5	Membrane thickness uniformity
6	Permeability to H ₂ and O ₂
7	Water Uptake and Dimensional Change
8	Thermogravimetric/DSC
9	Tensile Test

ElectroHyPEM - Membrane Specifications and Procedures

5.1 In-Plane Conductivity

Summary

Using a four electrode conductivity clamp (e.g. the Bekk Tech BT-110 Conductivity Clamp) in-plane conductivity can be determined by applying a specific current across a linear strip of membrane and measuring the resulting voltage. Four electrodes are used in order to separate voltage drop due to ion transport from that due to any electro-chemical reactions.

In-Plane Conductivity

Protocol and Metrics

Pre-conditioning	Membrane must be hydrated prior to measurement and the conductivity clamp immersed in a beaker of type 1 water.	
Operating conditions:		
Measurement technique	4 electrode chronopotentiometry	
Membrane sample size	At least 20mm long and less than 17mm wide.	
Water temperature	Controlled and recorded.	
Current	Appropriate current such that the voltage is between 0.01 and 1V	
Technique	<ul style="list-style-type: none"> • To test whether electrodes are making good electrical contact with the membrane and to determine the appropriate current, apply a linear voltage sweep across the two outer electrodes • Then in the four-electrode mode, apply the predetermined appropriate current for one minute to outer contacts or until a constant voltage is achieved, whichever is longer. • Measure voltage difference across inner electrodes • Using the applied current and resulting voltage, the resistance of the sample of membrane can be calculated $R = V/I$ <ul style="list-style-type: none"> • From the resistance of the membrane sample and the known dimensions of the sample, resistivity and conductivity can also be calculated. $\sigma = \frac{1}{\rho} = \frac{d_{contacts}}{L_{membrane} \times W_{membrane} \times R}$	
METRIC	FREQUENCY	TARGET
$\sigma_{membrane}$	As required	200 mS·cm ⁻¹ at 80°C

ElectroHyPEM Membrane Specifications and Procedures

5.2 Measurement of Membrane Ion-exchange Capacity and Equivalent Weight

Summary

A base titration is used to measure the number of equivalents of sulfonic acid groups within the polymer and the measurements used to calculate the ion-exchange capacity and equivalent weight of the membrane.

Measurement of Membrane Ion-exchange Capacity and Equivalent Weight

Protocol and Metrics

Membrane Conditioning

1. Treat samples with 0.1M sulfuric acid for 1 hr, at 30 °C.
2. Rinse the samples thoroughly with water and then soak in water for 1 hr, at 30 °C.
3. Dry the samples in a vacuum oven for 4 hrs, at 50 °C.

Test Conditions

Approximately 0.5 g of dried sample is required for the test.

1. Weigh the dried sample and record the mass to 4 dp.
2. Place the sample into 100 ml of 0.01M potassium hydrogen carbonate (aq) solution and leave to soak for 16 hrs, at room temperature.
3. Titrate the potassium hydrogen carbonate soak solution against 0.01M hydrochloric acid and record the volume of hydrochloric acid required to neutralize the potassium hydrogen carbonate soak solution.
4. Based on at least three runs, calculate the average volume of hydrochloric acid required to neutralize the potassium hydrogen carbonate soak solution.
5. Calculate the concentration of the potassium hydrogen carbonate soak solution following contact with the membrane.
6. Calculate the difference between the concentrations of the potassium hydrogen carbonate solution before and after contact with the membrane, to obtain the equivalent number of moles of sulfonic acid groups in the membrane.
7. Using the number of moles of sulfonic acid groups in the membrane and the mass of the dry membrane, calculate the ion-exchange capacity and equivalent weight of the membrane.

METRIC	FREQUENCY	TARGET
Ion-exchange Capacity	As required	No target for monitoring
Equivalent Weight	As required	No target for monitoring

ElectroHyPEM Membrane Specifications and Procedures

5.3 Membrane Chemical Stability – Fenton’s Test

Summary

This test gives an indication of the oxidative chemical stability of the membrane. A section of the membrane is held in an aqueous solution of 3% H₂O₂ and 4ppm Fe²⁺ at 80°C for 2 hours and the mass loss is determined from a comparison of dry mass before and after the test.

Membrane Chemical Stability – Fenton’s Test

Protocol and Metrics

Membrane Conditioning	Hydrate membrane according to standard hydration procedure, take stamp from central area, dry gently under vacuum (50°C for 4h) and measure the mass.	
Stamp size	4cm x 4cm	
Concentration of hydrogen peroxide	3% by weight	
Concentration of Fe²⁺	4ppm by weight	
Test Conditions - Volume	50ml	
Test Conditions - Temperature	80°C	
Test Conditions - Time	2hr	
Test Conditions	Wash the membrane thoroughly in type 1 water before drying the membrane under vacuum at 50°C for 4h. Measure the mass.	
Mass loss formula	Mass loss (%) = [(mass _{initial} – mass _{after})/mass _{initial}] \times 100	
Number of repeats	3	
METRIC	Conditions	TARGET
Mass Loss	average of 3 readings of mass loss to 4d.p.	No target for monitoring

ElectroHyPEM Membrane Specifications and Procedures

5.4 Membrane Hydrolytic Stability Test

Summary

A section of the membrane is held in water at 95°C for 24 hours and the mass loss is determined from a comparison of dry mass before and after the test. The IEC of the specimen is then measured and compared to the standard value for the membrane.

Membrane Hydrolytic Stability Test

Protocol and Metrics

Membrane Conditioning	Measurements taken with membrane conditioned to 23°C, 50% RH	
Specimen size	4cm x 4cm	
Test conditions	Immersed 24hr in 50ml Type 1 water at 95°C Dried in a vacuum oven at 50°C for 4hr Membrane mass measured before and after	
Number of repeats	5	
METRIC	FREQUENCY	TARGET
Mass loss	After 24 hours	No target for monitoring
IEC change	After 24 hours	No target for monitoring

ElectroHyPEM Membrane Specifications and Procedures

5.5 Measurement of Membrane Thickness and Uniformity

Summary

The thickness of a membrane specimen in the dry, humidified or hydrated state is the arithmetic mean of the values obtained from at least three dimension measurements (see table for recommended number of measurements) taken at different points across a membrane specimen, using a calibrated micrometer screw gauge capable of measurement to the nearest 2.5 μm . The uniformity of a membrane specimen is indicated by the maximum and minimum of the range of the dimension measurements.

Measurement of Membrane Thickness and Uniformity Protocol and Metrics

Membrane Conditioning

Dry state: 23 °C \pm 2 °C, 50% relative humidity

Humidified state: As appropriate. Must be recorded.

Hydrated state: As appropriate. Must be recorded.

Test Method

1. Prepare and condition each specimen as appropriate.
2. Close the micrometer on an area of the specimen that has a similar dimension to the one to be measured, but is not one of the measurement positions.
3. Observe this reading, and then open the micrometer approximately 100 μm beyond the expected reading and move the specimen to the measurement position.
4. Close the micrometer at such a rate that the scale divisions may be counted easily as they pass the reference mark. This rate is approximately 50 $\mu\text{m/s}$.
5. Continue the closing motion until contact with the specimen surface is just made as evidenced by the initial development of frictional resistance to movement of the micrometer screw. If using a micrometer fitted with a calibrated ratchet or friction thimble, continue the closing motion until the ratchet clicks three times or the friction thimble slips. Observe the indicated dimension.
6. If required, correct the observed indicated dimension using a calibration chart and record the corrected dimension value.
7. Move the specimen to another measurement position and repeat the steps 2 - 6.
8. Make and record at least three dimension measurements on each specimen (see table below for recommended number of measurements). The arithmetic mean of all dimension values is the thickness of the specimen.

Specimen Dimensions (cm)	Specimen Area (cm ²)	Recommended Number of Measurements
5 x 5	25	5
10 x 10	100	9
15 x 15	225	16
20 x 20	400	25

9. Record the maximum and minimum of the range of the dimension measurements taken. This is the uniformity of the specimen.

METRIC

FREQUENCY

TARGET

Membrane Thickness (μm)	As required	No target for monitoring
Membrane Uniformity (μm)	As required	$\pm 10\%$ of the mean thickness

ElectroHyPEM Membrane Specifications and Procedures

5.6 Membrane Permeability to Hydrogen Gas

Summary

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	100mV to 400mV
Scan rate	2mV/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 (5 ml/min) to keep membrane hydrated • Sweep cathode potential from rest potential (100mV) to 400mV against anode at 2mV/s • Report crossover rate at 300mV

METRIC	FREQUENCY	TARGET
Hydrogen crossover current		<1mA/cm ²
Hydrogen crossover rate		<0.070 ml/min/cm ² hydrogen

ElectroHyPEM - Membrane Specifications and Procedures

5.7 Water Uptake and Linear Expansion

Summary

The hydration of membranes can be characterized by comparing the weight and size of dry samples with that of hydrated samples. From these measurements, water uptake and dimensional change can be calculated.

Water uptake and linear expansion

Protocol and Metrics

Pre-conditioning	Samples of the membrane should be dried in an oven to constant weight.
Operating conditions:	
Measurement technique	A balance capable of measuring to 0.0001g. Calipers capable of measuring 0.01mm
Membrane sample size	Approximately 20mm x 10mm.
Hydration temperature	30°C, 60°C and 90°C
Technique	<ul style="list-style-type: none"> • A minimum of three samples should be used for each test. • The size and weight of pre-conditioned samples are determined. • The samples are then placed in containers of deionised water and placed in an oven at the appropriate temperature for 24 hours. • After 24hrs, the samples are removed from the oven and measurements of length and weight are taken.
Analysis	<ul style="list-style-type: none"> • % Water Uptake = $((\text{hydrated mass} - \text{dry mass}) / \text{dry mass}) * 100$ • % Linear Expansion = $((\text{hydrated length} - \text{dry length}) / \text{dry length}) * 100$

METRIC	FREQUENCY	TARGET
Water Uptake	As required	No target
Linear Expansion	As required	No target

ElectroHyPEM Membrane Specifications and Procedures

5.8 Thermogravimetric/DSC Testing

Summary

This test gives an indication of the chemical and thermal stability of the membrane.

Thermogravimetric/DSC Testing

Protocol and Metrics

Membrane Conditioning	Hydrate MEA according to standard hydration procedure,
Equipment	TA Instruments Q2000 DSC, Q500 TGA or similar
Atmosphere	Nitrogen/Air
Temperature Range	25°C to 900°C
Heating Ramp	2°C/min
Logging Frequency	1Hz
Number of repeats	3

METRIC	Conditions	TARGET
Start of Thermal Decomposition		No target for monitoring

Glass Transition Temperature

Protocol and Metrics

Membrane Conditioning	Hydrate MEA according to standard hydration procedure,
Equipment	TA Instruments Q800 DMA or similar
Atmosphere	Air
Temperature Range	25°C to 400°C
Heating Ramp	2°C/min
Logging Frequency	1Hz
Number of repeats	3

METRIC	Conditions	TARGET
Glass Transition Temperature T _g	At maximum of tan(δ)	No target for monitoring

ElectroHyPEM Membrane Specifications and Procedures

5.9 Tensile Testing

Summary

This test gives an indication of the mechanical properties of the membrane and it is based on ASTM D882-09 Tensile Properties of Thin Plastic Sheeting. As the machine does not have an environmental chamber, the test will be performed submerged in a water bath.

Tensile Testing

Protocol and Metrics

Membrane Conditioning	Hydrate MEA according to standard hydration procedure
Equipment	Instron 3344 or similar
Stamp size	Dumbell shaped stamp similar to Type IV in ASTM D638-10. Width of narrow section = 6mm Length of narrow section = 33mm Gauge length = 25mm Distance between the tabs = 65mm Length overall = 115mm Radius of fillet = 14mm Outer radius = 25mm
Initial Grip Separation	60mm
Initial Strain Rate	0.5mm/mm.min
Rate of Grip Separation	30mm/min (Rate of Grip Separation = Initial Strain Rate x Initial Grip Separation)
Load cell	Suitable for material tested
Water bath temperature	23°C ± 1°C
Number of repeats	5 (in each direction if the sample is anisotropic)

METRIC	Frequency	TARGET
UTS (MPa to 3 significant figures)	As required	No target for monitoring
Elongation at break (% to 2 significant figures)	As required	No target for monitoring
Young's Modulus (MPa to 3 significant figures)	As required	No target for monitoring

6.0 MEA characterization under project relevant conditions

Summary of Procedures

Procedures	
Number	Test
1	MEA Accelerated Cycling Test
2	MEA Steady-State Test at 1A/cm ²
3	MEA Steady-State Test at 2A/cm ²
4	MEA Hydration Procedure
5	Measurement of Current-Voltage Curve
6	Measurement of Catalyst Surface Area
7	Measurement of Through-Plane Conductivity
8	MEA Hydrogen Crossover Test
9	MEA Water Analysis Procedure

ElectroHyPEM MEA Specifications and Procedures

6.1 MEA Accelerated Cycling Test

Summary

MEAs are tested under a load cycle at constant temperature and pressure to test degradation mechanisms occurring under a dynamic load.

MEA Accelerated Cycling Test Protocol and Metrics

Membrane Conditioning	Refer to MEA Hydration Procedure	
Test Conditions	Single cell 8 – 300 cm ² 1. Before starting test operate for 24 hrs at steady-state, 1A/cm ² . 2. Measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm ² – 2 A/cm ²). 3. Followed by a 4 step cycle: <ul style="list-style-type: none"> • Step 1: 1 min at 1 A/cm² • Step 2: 1 min at 2 A/cm² • Step 3: 1 min at 1 A/cm² • Step 4: 1 min at 0 A/cm² 4. At the end of the test, measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm ² – 2 A/cm ²).	
Number of Cycles	1500	
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 300 cycles	No target for monitoring
Hydrogen Cross-over	After 24 hrs of steady-state operation at the beginning of the test. Following 1500 cycles	≤1 mA/cm ² at targeted operating temperatures
Operating Voltage	Continuous	≤1.6 V at 1A/cm ² ≤1.8 V at 2 A/cm ²
IV Curve	After 24 hrs of steady-state operation at the beginning of the test. Before stopping the test.	No target for monitoring

ElectroHyPEM MEA Specifications and Procedures

6.2 MEA Steady-State Test at 1 A/cm²

Summary

MEAs are tested under constant load, temperature and pressure, to measure the rate of MEA degradation at 1 A/cm².

MEA Steady-State Test at 1 A/cm²

Protocol and Metrics

MEA Conditioning	Refer to MEA Hydration Procedure	
Test Conditions	Single cell 8 – 300 cm ² <ol style="list-style-type: none"> 1. Before starting test, operate for 24 hrs at steady-state, 1 A/cm². 2. Measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm² – 1 A/cm²). 3. Operate the cell at a steady-state 1 A/cm². 4. At the end of the test, measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm² – 1 A/cm²). 	
Total Time	1000 hrs after measurement of the first IV 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	After 24 hrs of steady-state operation at the beginning of the test. Every 100 hrs after the first IV curve.	No target for monitoring
Hydrogen Cross-over	After 24 hrs of steady-state operation at the beginning of the test. Following 1000 hrs of operation	≤1 mA/cm ² at targeted operating temperatures
Operating Voltage	Continuous	≤1.6 V
Voltage Degradation	1000 hrs of operation after first IV curve.	≤ 15 μV/hr degradation in operating voltage using line of best fit.
IV Curve	After 24 hrs of steady-state operation at the beginning of the test. Before stopping the test.	No target for monitoring

ElectroHyPEM MEA Specifications and Procedures

6.3 MEA Steady-State Test at 2 A/cm²

Summary

MEAs are tested under constant load, temperature and pressure, to measure the rate of MEA degradation at 2 A/cm².

MEA Steady-State Test at 2 A/cm²

Protocol and Metrics

MEA Conditioning	Refer to MEA Hydration Procedure	
Test Conditions	Single cell 8 – 300 cm ² <ol style="list-style-type: none"> 1. Before starting test, operate for 24 hrs at steady-state, 1 A/cm². 2. Measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm² – 2 A/cm²). 3. Operate the cell at a steady-state 2 A/cm². 4. At the end of the test, measure an IV curve as detailed in the Measurement of Current-Voltage Curve Procedure (Current Range: 0.5 mA/cm² – 2 A/cm²). 	
Total Time	1000 hrs after measurement of the first IV 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	After 24 hrs of steady-state operation at the beginning of the test. Every 100 hrs after the first IV curve.	No target for monitoring
Hydrogen Cross-over	After 24 hrs of steady-state operation at the beginning of the test. Following 1000 hrs of operation	≤1 mA/cm ² at targeted operating temperatures
Operating Voltage	Continuous	≤1.8 V
Voltage Degradation	1000 hrs of operation after first IV curve.	≤ 15 μV/hr degradation in operating voltage using line of best fit.
IV Curve	After 24 hrs of steady-state operation at the beginning of the test. Before stopping the test.	No target for monitoring

ElectroHyPEM MEA Specifications and Procedures

6.4 MEA Hydration Procedure**Summary**

In order to ensure that the MEA is hydrated and no pollutants are released from the MEA, this procedure should be done after the appropriate rinsing of the MEA as a final check.

MEA Hydration Procedure**Protocol and Metrics**

MEA Conditioning	Hydrate the MEA at the operating temperature for 24h before analysis	
Volume of water	2ml of Type 1 water per cm ² of membrane	
Method of testing	For sampling, please refer the Water Analysis protocol	
Outcome - Pass	If the water passes the targets, the MEA is ready to be used	
Outcome - Fail	If the water does not pass the targets, discard the water; continue rinsing the MEA as appropriate before repeating the procedure above.	
METRIC	FREQUENCY	TARGET
TOC	24h until it passes	<0.3ppm
pH	24h until it passes	Between 5 and 7
Conductivity	24h until it passes	<1.5µS/cm
Fluoride	24h until it passes	<0.1ppm
ICPMS	24h until it passes	<100µg/L for all elements apart from Si which is <500µg/L

ElectroHyPEM MEA Specifications and Procedures

6.5 Measurement of Current-Voltage Curve**Summary**

This is a measure of the cell voltage as a function of the applied current. The current is raised and then lowered to measure any hysteresis. It is a quick measure of the MEA performance and can give insights into both the membrane resistance and the catalytic activity. At low currents the pressure must be at ambient to ensure the percentage of one gas in another stays well below flammability limits.

IV Curve**Protocol and Metrics**

Pre-conditioning	MEA must be hydrated prior to measurement It is recommended that cells run for at least 24 hours to ensure the MEA has reached a steady state	
Operating conditions:		
Control	Chronopotentiometric (current controlled; voltage recorded)	
Cell size	As appropriate (but must be recorded)	
Water temperature	Recorded on both exits and reported with IV 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 range	0.5 mA·cm ⁻² to 2 A·cm ⁻² (and reversed)	
Step size	Smaller at low currents such that the change in voltage between step size is < 30 mV (see example below)	
Technique	<ul style="list-style-type: none"> • Hold current at 100 mA·cm⁻² for 5 minutes to ensure catalysts are in the correct oxidation state • Step current to 0.5 mA·cm⁻² • Record voltage after 1 min (Note: if dV/dt > 1mV·cm⁻²·s⁻¹ then must wait until dV/dt < 1mV·cm⁻²·s⁻¹ before recording voltage) • Step to next current and repeat . 	
METRIC	FREQUENCY	TARGET
I-V curve	Start and end of any test plus as required	
Voltage at 1 A/cm ²		1.6 V
Voltage at 2 A/cm ²		1.8 V

ElectroHyPEM MEA Specifications and Procedures

Example of applied current densities against which voltage should be recorded:

Current Density [A·cm ⁻²]	Cell Voltage [V]	Current Density [A·cm ⁻²]	Cell Voltage [V]
0.0005		0.45	
0.001		0.5	
0.002		0.6	
0.005		0.7	
0.01		0.8	
0.02		0.9	
0.03		1	
0.04		1.1	
0.06		1.2	
0.08		1.3	
0.1		1.4	
0.15		1.5	
0.2		1.6	
0.25		1.7	
0.3		1.8	
0.35		1.9	
0.4		2	

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

ElectroHyPEM MEA Specifications and Procedures

6.6 Measurement of Catalyst Surface Area**Summary**

This is an approximate measure of the catalyst surface area. Unlike fuel cells, the catalytic surface area within an electrolyser MEA is difficult to measure. This difficulty can be attributed to the pseudocapacitive behavior exhibited by the oxygen evolution catalysts. However this procedure is proposed as a comparative measure to understand changes in amount of catalyst surface area due to erosion or other means of catalyst decay.

Measurement of Catalyst Surface Area**Protocol and Metrics**

Pre-conditioning	MEA must be hydrated prior to measurement	
Operating conditions:		
Measurement technique	Cyclic voltammetry	
Cell size	As appropriate (but must be recorded)	
Water temperature	Recorded on anode exit and reported	
Pressure	Pressure must remain at atmospheric pressure	
Cell setup	<ul style="list-style-type: none"> • Hydrogen on negative electrode, water flowing on positive electrode • RE and CE connected to negative electrode; WE connected to positive electrode 	
Voltage range	0V to 1.4V (and reverse), cycle twice second cycle analysed	
Scan rate	20 mV·sec ⁻¹	
METRIC	FREQUENCY	TARGET
Positive charge (integration of the positive current)	As required	No target for monitoring

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6.7 Measurement of Through-Plane Conductivity

Summary

The measurement of through plane conductivity is performed using controlled current electrochemical impedance spectroscopy (PEIS). Although low frequency measurement is not necessary for membrane resistance, it provides other useful information about the MEA. However, to do this a model needs to be developed that encompasses the *physical* and *chemical* characteristics of the system whilst being the most *parsimonious* for the data. Although primarily a measure of membrane resistance, an MEA needs to be constructed to perform this properly.

Measurement of Through-Plane Conductivity

Protocol and Metrics

Pre-conditioning	MEA must be hydrated prior to measurement	
Operating conditions:		
Measurement technique	Potentiostatic Electrochemical Impedance Spectroscopy (PEIS)	
Cell size	As appropriate (but must be recorded)	
Water temperature	Recorded on both exits and reported	
Pressure	Pressure must remain at atmospheric pressure	
Frequency range	50 kHz to 100 MHz (10 steps/decade)	
DC current	10 mA·cm ⁻² ; 20 mA·cm ⁻² ; 50 mA·cm ⁻² ; 100 mA·cm ⁻²	
AC current	10 % of applied DC current	
Technique	<ul style="list-style-type: none"> • Hold current at 100 mA·cm⁻² for 5 minutes to ensure catalysts are in the correct oxidation state • Step current to 10 mA·cm⁻² for 1 min • Perform PEIS at 10 mA·cm⁻² from 50 kHz to 100 MHz (10 steps/decade) • Repeat for other currents 	
Analysis	<ul style="list-style-type: none"> • Plot each result in standard Nyquist form • Where the signal first crosses the real axis is the resistance (high frequency resistance) • Subtract cell resistance $R_{\text{membrane}} = R_{\text{measured}} - R_{\text{cell}}$ <ul style="list-style-type: none"> • Normalise by geometric area (MEA) $R_{\text{area specific}} = R_{\text{membrane}} \times GA_{\text{MEA}}$ <ul style="list-style-type: none"> • Calculate conductivity using hydrated thickness of membrane $\sigma_{\text{membrane}} = T_{\text{membrane}} / R_{\text{area specific}}$	
METRIC	FREQUENCY	TARGET
σ_{membrane}	As required	200 mS·cm ⁻¹ at 80°C

ElectroHyPEM MEA Specifications and Procedures

6.8 MEA Hydrogen Crossover Test

Summary

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. This test requires that there are no recombination catalysts (e.g. Pt) at the anode side of the MEA (unless specifically included to reduce crossover).

MEA Hydrogen Crossover Test

Protocol and Metrics

Assembly	MEA in standard electrolysis cell with water flowing, no Pt at anode	
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 10MPa delta P, 2.5MPa increment	
Current Density	1A/cm ²	
METRIC	FREQUENCY	TARGET
%H ₂ in O ₂	Steady state measurement	<1%
Quote thickness, temperature, current density, pressure alongside values		

ElectroHyPEM MEA Specifications and Procedures

6.9 MEA Water Analysis Procedure

Summary

This is a general procedure for the analysis of water.

MEA Water Analysis Procedure

Protocol and Metrics

Where to take samples	Take water samples from the O ₂ , H ₂ and inlet stream	
Sampling for TOC, pH, Conductivity and Fluoride Analysis	100ml in a glass bottle	
Sampling for ICPMS	10ml in a 15ml plastic centrifuge tube	
Equipment for TOC analysis	OI Analytics 1030W or equivalent system	
Equipment for pH, conductivity and fluoride analysis	Mantech Titrasip System with conductivity probe, pH probe and fluoride ISE or equivalent system	
Equipment for ICPMS analysis	Agilent 7500cx ICPMS or equivalent system	
Method for TOC analysis	Wet (persulfate) oxidation TOC and TIC measurement (averaged over 3 repeats)	
Method for pH, conductivity and fluoride analysis	Single Conductivity and pH measurement, averaged fluoride measurement (3 repeats) Acidification with Traceselect Ultra Nitric acid to ~5%.	
Method for ICPMS analysis	Quantitative measurement of the following elements; Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Zr, Mo, Ru Ce, Ta, Ir, Pt, Pb.	
METRIC	FREQUENCY	TARGET
TOC	As required	As appropriate to the test being analysed
pH	As required	Between 4 and 7
Conductivity	As required	As appropriate to the test being analysed
Fluoride	As required	As appropriate to the test being analysed
ICPMS	As required	As appropriate to the test being analysed

7. Table 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/support formulation			
Batch No			
Application as anode or cathode			
Bulk and possibly surface composition			
Physico-chemical parameters: structure			
Physico-chemical parameters: particle size/crystallite size	nm		
Support oxidation charge in electrochemical tests at 1.4 V x 2h.	mC/g; mC / cm ² BET		
Support surface area retention after an accelerated test at 2.2 V vs. RHE x2h	%		
Electrochemically active surface area	m ² /g; mC/mg mC cm ⁻² mF mg ⁻¹ mF cm ⁻²		
OER overpotential (IR-free) at 1 A cm ⁻² at specific loading (mg cm ⁻²) in the presence of specific electrolyte, temperature (°C) and pressure (bar) conditions	mV		
Cathode overpotential vs. RHE at 1A cm ⁻² at specific loading (mg cm ⁻²) in the presence of specific electrolyte, temperature (°C) and pressure (bar) conditions	mV		
Stability: Electrochemical surface area loss in accelerated tests vs. initial conditions	%		

MEA:

	unit	result	method
MEA formulation (anode, cathode, membrane, diffusion layers)			
Batch No			
Overall PGM loading in the MEA			
Performance at 1 A cm ⁻² at specific temperature (°C) and pressure (bar) conditions	V		
Performance at 2 A cm ⁻² at specific temperature (°C) and pressure (bar) conditions	V		
Performance degradation in steady-state tests at 1 A cm ⁻² or under different current density (t.b.d) 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 Cross-over 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	Ohm cm ²		
Series resistance at specific current density or voltage, at specific temperature (°C) and pressure (bar) conditions	Ohm cm ²		
Polarization resistance at specific current density or voltage, at specific temperature (°C) and pressure (bar) conditions	Ohm cm ²		

8. Conclusions

The procedures reported here will be used to screen active components and as means of verification to assess the achievement of project milestones. In general, these procedures will provide a systematic approach to test materials and components in order to validate them for PEM electrolysis applications.

The aim is to assess each component by specific testing procedure in order to deconvolute the properties of each component. This allows identification of specific interface drawbacks and will address the materials development towards the best combination of membrane, electrocatalysts and assembling procedures.

The obtained data will be presented in table form and will allow comparison of the results from different laboratories.