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New Anion Exchange Membrane Electrolysers

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Anion Exchange Membrane Electrolysis for Renewable Hydrogen Production on a Wide-Scale

# ANIONE – Deliverable Report

## D2.1 – Harmonised test protocols for assessing AEM electrolysis components, cells and stacks in a wide range of operating temperature and pressure

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## Summary

The objectives of the deliverable D2.1 are to define characterisation and test protocols for the assessment of performance, efficiency and durability of the newly developed AEM electrolyser components and stack.

The procedures and methods defined within are a set of protocols for ex-situ and in-situ characterisation of active components such as membranes, catalysts, electrode-membrane assemblies (MEAs) and stacks. Included are steady-state and dynamic-mode durability tests as well as performance evaluation under specific operating conditions.

In particular, the procedures deal with an establishment of a set of characterisation and testing protocols for *ex-situ* and *in-situ* characterisation of AEM electrolyser components such as membrane, electro-catalysts and MEAs. The testing protocols, parameters and procedures for the assessment of these active components are defined to allow for a homogeneous screening and evaluation of the newly developed components. Appropriate testing protocols are defined to individually screen materials in order to find those that provide the perspectives of application in large area MEAs and thus in the final stack. The procedures for active components are complemented by measurement protocols for stack assessment.

All these procedures and protocols will be used to validate the quantitative project targets in terms of performance, durability and dynamic behaviour.

Baseline components against which progress is assessed, in terms of durability and performance cost, are identified.

# Abbreviations

| | |
|---|---|
| AEM | Anion Exchangeable Membrane |
| ASP | Area Specific Resistance |
| BET | Specific Surface Area measured by the Brauner–Emmett–Teller method |
| BoT | Beginning-of-Test |
| d.p. | Decimal precision |
| DHE | Dynamic Hydrogen Electrode |
| DMA | Dynamic Mechanical Analysis (Glass transition temperature) |
| DoA | Description of Action |
| DSC | Differential Scanning Calorimeter |
| Ea | Anode Overpotential |
| Ec | Cathode overpotential |
| ECSA | ElectroChemical Surface Area |
| EDX | Energy Dispersive X-ray |
| EIS | Electrochemical Impedance Spectroscopy |
| EoT | End-of-Test |
| EW | Equivalent weight |
| GC | Gas Chromatography |
| GDL | Gas Diffusion Layer |
| ICP | Inductively Coupled Plasma |
| IEC | Ion Exchange Capacity |
| MEA | Membrane Electrode Assembly |
| OCV | Open Cell Voltage |
| PEM | Proton Exchangeable Membrane |
| PTL | Porous Transport Layers |
| RHE | Reversible Hydrogen Electrode |
| RT | Room Temperature |
| SEM | Scanning Electron Microscopy |
| TEM | Transmission Electron Microscopy |
| TGA | Thermogravimetric Analysis |

## Contents

# 1 Introduction

This deliverable aims at implementing for Anion Exchange Membrane Electrolysis the harmonised terminology, procedures and characterisation protocols developed by JRC with internally defined protocols and the joint protocols agreed among three H2020 FCH JU projects i.e., ANIONE, CHANNEL and NEWLY.
Another objective is regarding the identification of a benchmark of baseline components against which progress may be assessed in terms of durability and performance.

Regarding the test procedures special regard is addressed to the operating conditions in terms of operating temperature, pressure and feed mode.
Protocols and procedures here defined concern with:
- Ex situ and in situ characterisation membranes, catalysts, electrodes, MEAs and stack hardware components:
- Characterisation and testing protocols to assess stack durability in steady-state and dynamic mode.
- Establish a benchmark of baseline components against which progress may be assessed in terms of durability, performance and cost.

The definition of these protocols will serve as an input for both the harmonization efforts and to provide input to subsequent specification work as well as to enable planning of the test activities in WP3, WP4, WP5 and WP6.
Accordingly, test protocols, parameters and procedures here defined will be used to screen the best performing membranes, anode and cathode catalysts, as well as MEAs prepared obtained using different methods. These will also include a set of procedures for ex-situ physico-chemical characterisation for the novel components since the analytical procedures carried out in the different laboratories require harmonisation to allow a comparison of the results achieved by the different partners. Specific protocols will regard an assessment of the dynamic behaviour using specific current profiles. The effects caused by such intermittent operation will be identified to establish the performance decay and compare it with the effects recorded for competing electrolysis technologies.
Implementation of these procedures will thus allow validating the quantitative project targets in terms of performance, durability and dynamic behaviour in a wider range of temperature and pressure conditions.

## 2 PROTOCOLS

### 2.1 MEMBRANE ASSESSMENT

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 ageing in alkaline solution and the Fenton reactions in the liquid phase, especially for perfluorinated membranes, hydrolytic stability, equivalent weight, gas permeability, water uptake and dimensional change, differential scanning calorimetry and mechanical properties by tensile strength measurements.
A set 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 AEM 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.

Membranes can be characterised in halide (e.g. bromide or chloride for the benchmark membrane), tosylate or hydroxide forms. This should be specified. Being the final use in hydroxide form a pre-treatment of the final membrane before measurements is herewith identified:

The membranes should be exchanged with hydroxyl ions before characterisation according to the following prescription:

· exchanged for 24 hrs in KOH 1M solution at room temperature
· rinse in demineralised water until neutral pH
· dab between filter papers and store in a closed bag in wet form

### 2.1.1 First set of testing procedures for membranes - 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 or KOH at the temperature of 50°C: the sample must not dissolve or swell excessively (<30%).
- no leach-out of functional groups as determined by IEC measurement (<1%). Refer to section 2.1.7.2 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*: anionic membrane processing with 1 M NaCl at room temperature for 72 hrs with subsequent exchange for 24 hrs in KOH 1M solution at room temperature followed by titration.

Data to be reported in meq/g (3 d.p.), 1 eq = 1 mol of $NR_4^+$

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. up to 120°C or the maximum temperature, in steps of 10°C), pressure (ambient pressure and eventually pressurised mode 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, chronopotentiometry or AC impedance with 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 $H_2$ and $O_2$ gases at various pressures and differential pressures.

- *Water uptake*: A rigorous procedure is indicated in section 2.1.7.7 For pre-screening, a simple approach is here reported: equilibration for 2 h under specific conditions, removal of solvent from surface by filter 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 2 h in water at the relevant temperature in a closed glass or plastic bottle. See also section 2.1.7.7

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 in oven at 80°C under vacuum 2 hrs

*% Linear Expansion Coefficient (LEC)* is defined by:

% LEC = ((hydrated length – dry length) / dry length) *100

*% Water Uptake (WU)* is defined by:

% WU = ((hydrated mass – dry mass) / dry mass) *100

*% Water Content ($\lambda$)* is defined by:

$\lambda$ = ((WU/18) *10)/ IEC

-*$H_2$ and $O_2$ permeability* measured by using specific sensors; alternatively, $H_2$ permeation it may be also determined in-situ under differential pressure using the conventional electrochemical methods (see section….).
- *Chemical and thermal stability* (TGA-DSC): RT to 900°C in air or nitrogen atmosphere at a heating rate of 5°C/min.
- *Glass transition temperature* (DMA): from RT to 400°C in air at a heating rate of 2°C/min, frequency 1 Hz, Tg 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 dataset.

### 2.1.3 Third set - Characterisation under project relevant conditions

- *Membrane characterization under balanced or differential pressure conditions*: a pressurised cell is used. This cell can be pressured hydrostatically up to 30 bar. The membrane can be eventually incorporated in a membrane-electrode assembly (MEA) and gas diffusion media.
  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 and with recirculation of KOH.
- *Ex-situ Chemical Stability* in concentrated (1 M) or diluted (0.1 M) KOH solution
- *Oxidative Stability for perfluorinated systems:*
  The Fenton test is usually not used as a stability test of anionic membranes to investigate the formation of radicals. Because iron in a basic environment precipitates as colloidal hydroxide according to the Pourbaix diagram. This may result into the decomposition of $H_2O_2$ into $H_2O$ and $O_2$ without production of radicals. Actually, the Fenton test is carried out in acidified $H_2O$ / $H_2O_2$. The Fe-catalyzed radical chemical degradation is therefore not an active mechanism in a basic system.
  However, it is not completely unusual to find in the literature that a Fenton test is anyway carried out to verify the stability in an oxidizing environment of an anion exchange membrane [Sharma et al. Journal of Membrane Science Volume 563, 1 October 2018, Pages 561-570]. The oxidative stability of the AEM is generally conducted at mild temperature for several hours and the membrane stability is assessed in terms of weight loss and change of IEC. Since some weight loss has been recorded in

previous Fenton tests of AEM membranes, these data can provide information on the stability of membrane over a harsh oxidative environment. It is however, appropriate to make the pH slightly acidic during the experiment by adding HCl until reaching a pH=3. The hydroxyl ions are replaced by $Cl^-$. This has no relevant impact on the oxidative stability of the membrane.

- Fenton's Reagent Test - 3% $H_2O_2$, 4 ppm $Fe^{2+}$ ions, in the presence of a pH=3 by addition of diluted HCl, at 60°C for 4 h. Measure mass loss and check the fluoride release for perfluorinated anionic membranes during vs. time immersing by $F^-$sensitive electrode.
- *Hydrolytic Stability*: Hot Water Solubility Test – Pure water, at 90°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 In-situ MEMBRANE ASSESSMENT

*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 ($H_2$).

Cross-over measurements are carried out *in-situ* under relevant temperature and pressure conditions by using chromatographic analysis, sensor method or electrochemical methods if applicable.
Electrochemical crossover test is carried out according to the procedure reported below:
Assemble MEA with the membrane under investigation and Pt/C electrodes.
Assemble cell with potentiostat to control voltage and measure current

Specifically, for cross-over measurements, flow 100% humidified hydrogen on cathode electrode (equiv. of 1.5 stoich at 1 A/cm$^2$), 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/cm$^2$ hydrogen) under steady state.
Possibly measure as a function of temperature, ΔP, humidity, thickness.

### 2.1.5 Baseline (benchmark) membranes:

**FUMATECH (Fumasep FAA-3-50) membrane and ionomer dispersion.**

The FAA3-50 membrane (FumaTech), based on a brominated polysulfone backbone with quaternary ammonium side chain groups provided in bromide form, was subjected to anion exchange process and characterised for this application.
https://fuelcellstore.com/spec-sheets/fumapem-faa-3-50-technical-specifications.pdf

More details about the membrane properties can be found in Carbone et al. International Journal of Hydrogen Energy 45, (1620) 2020, 9285-9292.

Or

**EVONIK AEM membrane and ionomer dispersion**

A non-disclosure agreement with the supplier needs to be agreed before using this membrane as benchmark.

### 2.1.6 Dataset for membranes

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 fingerprint 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. In situ ohmic resistance associated to the membrane is determined from high frequency intercept on the real axis of the Nyquist plot obtained from AC-impedance spectroscopy after subtraction for a blank cell based on the same components but without the membrane.

### 2.1.7 ANIONE Membrane Specifications and Procedures:

Specific details for the ANIONE Membrane Specifications and Procedures are provided below with regard to some relevant membrane assessment procedures that are of primary interest for electrolysis applications

*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 |

#### 2.1.7.1 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 addition, the true $OH^-$ conductivity, the effect of temperature and the degree of hydration on membrane stability can be measured. The true conductivity measurement is carried out starting with a membrane having $CO3^{2-}$ as counter ion, as reported in the figure 1. The in-situ electrolysis can replace carbonate ions with $OH^-$ making the membrane conductive only by $OH^-$.

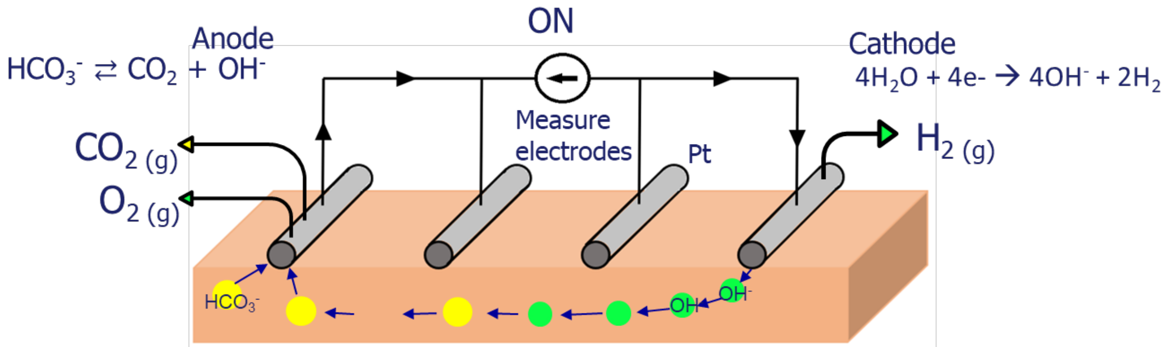


Figure 1 Scheme of the measurement of "true" hydroxide conductivity, reported in the paper: Noga Ziv, Dario R. Dekel, A practical method for measuring the true hydroxide conductivity of anion exchange membranes, Electrochemistry Communications 88 (2018) 109–113.

## 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:** | Measurements were carried out in the range of temperature 30-120°C, after a conditioning day at 30°C flowing humidified $N_2$ (100% RH) at room pressure or under a small pressure to avoid boiling water. |
| **Measurement technique** | The in-plane anion conductivity of samples with different counterions ($Cl^-$, $OH^-$, $CH_3C_6H_4SO_3^-$) is carried out by a four electrodes method by |
| **Measurement technique** | 4 electrode chronopotentiometry or electrochemical Impedance Spectroscopy (EIS). |
| **Membrane sample size** | At least 20mm long and less than 17 mm wide. |
| **Water temperature** | Controlled and recorded. |
| **Chronopotentiometry Technique** | • Appropriate current such that the voltage is between 0.01 and 1V<br>• 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<br>• 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.<br>• Measure voltage difference across inner electrodes<br>• Using the applied current and resulting voltage, the resistance of the sample of membrane can be calculated<br>$R = {}^{V}\!/_{I}$<br>• From the resistance of the membrane sample and the known dimensions of the sample, resistivity and conductivity can also be calculated.<br>$\sigma = \frac{1}{\rho} = \frac{d_{contacts}}{T_{membrane} \times W_{membrane} \times R}$ |
| **AC-impedance Technique** | • EIS parameters for the measurement are: 100 KHz - 1 Hz of frequency range and a 50 mV of amplitude |
| **True $OH^-$ conductivity** | • Application of constant direct current of 100 µA at platinum electrodes on the carbonated membrane for 30 min.<br>• Cathode: $OH^-$ production from water supplied by humidified inert gas ($N_2$ 99.9%), $H_2$ evolution<br>• Anode: $CO_2$, $O_2$ evolution<br>• Put current OFF and determine ionic resistance of the membrane in $HCO_3^-/OH^-$ form by EIS<br>• Follow the replacement of $HCO_3^-$ by $OH^-$ until reaching the minimum resistance value<br>• Determine the ionic resistance of the membrane in pure $OH^-$ form and any modification with temperature and time (EIS) |
| **Data treatment** | Activation energy was calculated by the Arrhenius law from conductivity results. |

The effective anion mobility is calculated as follows:

$\mu = \sigma / [A^-]\ F$
Where:

$\mu$ is the mobility, expressed in $cm^2/Vs$

$\sigma$ is the anion conductivity, expressed in S/cm

$[A^-]$ is the anion concentration

F is the Faraday constant (96485 C/mol)

The anion diffusion coefficient ($cm^2/s$) in water is calculated as follows:

$D_\sigma = \sigma RT / [A^-]\ F^2$

Where $\sigma$ is the anion conductivity of the hydroxide or chloride form measured in humidified Nitrogen;

R is the universal gas constant (8.31 $J\ mol^{-1}\ K^{-1}$)

T is the absolute temperature (K)

$[A^-]$ is the anion concentration

F is the Faraday constant

| METRIC | FREQUENCY | TARGET |
|---|---|---|
| $\sigma_{membrane}$ | As required | ≥50 $mS \cdot cm^{-1}$ at T ≤90°C |
| ***ASR*** (area specific resistance) | As required | ≤70 mOhm $cm^2$ at T ≤90°C |

### 2.1.7.2 Measurement of Membrane Ion-exchange Capacity and Equivalent Weight

**Summary**

A base titration is used to measure the number of equivalents of quaternary ammonium 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 1 M KOH for 24 hr, at 30°C.<br>2. Rinse the samples thoroughly with water and then soak in water for 1 hr, at 30°C.<br>3. Dry the samples in a vacuum oven for 2 hrs, at 50°C. |
| **Test Conditions** | A) Membrane in chloride form - Volhard method: membrane samples using $Cl^-$ as a counter-ion, after an exchange in NaCl 1M solution (72 h).<br>Approximately 0.1 g of dried sample is required for the test.<br>1. The dried membrane is immersed in $NaNO_3$ 0.1M for 48 hrs at room temperature, then it is removed.<br>2. The remaining solution is treated with 5 ml of $AgNO_3$ 0.1 M and 5 drops of $Fe(NO_3)_3$ (11 wt%).<br>3. A back-titration of the solution with KSCN 0.1M was performed. The amount of volume of the KSCN needed to achieve the so-called equivalent point ($V_{KSCN\ e.p.}$) was determined.<br>4. The IEC is calculated as follows:<br>IEC=(VAgNO3-VKSCNe.p.) [KSCN]/mdry<br>Where:<br>$V_{AgNO3}$ is the initial volume, expressed in ml<br>$V_{KSCN}$ e.p is the volume of the titrant at the equivalent point expressed in ml<br>[KSCN] is the concentration of titrant, expressed in molarity<br>mdry is the dry mass of the sample determined at 50°C for 2 hrs under vacuum (1,000 mbar), expressed in grams.<br><br>B) Membrane in hydroxide form - Acid-base back-titration<br>1. membrane is exchanged for 24 hrs in KOH 1M solution at room temperature<br>2. Afterwards, a dried sample is immersed in HCl 0.01M solution for 24 hrs at room temperature and removed.<br>3. The solution is back-titrated with NaOH 0.01M, using an automatic titrator.<br>4. The IEC was calculated as follows:<br>$IEC=(V_{HCl}-V_{NaOHe.p.})\ [NaOH]/m_{dry}$<br>Where:<br>$V_{HCl}$ is the initial volume, expressed in ml<br>$V_{NaOHe.p}$ is the volume of the titrant at the equivalent point expressed in ml<br>[NaOH] is the concentration of titrant, expressed in molarity |

$m_{dry}$ is the dry mass of the sample determined at 50°C for 2 hrs under vacuum (1,000 mbar), expressed in grams.

5. The final IEC value iscalculated from the average of three different measurements.

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

### 2.1.7.3 Membrane Chemical and oxidative Stability

**Summary**

This test gives an indication of the chemical and oxidative stability of the membrane. The first test refers to the hydroxide stability. The second test to the oxidative stability. A section of the membrane is held in an aqueous solution of 3% $H_2O_2$ and 4ppm $Fe^{2+}$ 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 – Ageing in hydroxide solution

### Protocol and Metrics

| | |
|---|---|
| **Membrane Conditioning** | Hydrate membrane according to standard hydration procedure, take stamp from central area, dry gently under vacuum (50°C for 2 h) and measure the mass. |
| **Stamp size** | 4cm x 4cm |
| **Area specific resistance (BoT)** | Measure conductivity as specified in 2.1.7.1 using ac-impedance. Determine area specific resistance (ASR) from the high frequency intercept. |
| **Concentration of KOH** | 0.1 M |
| **Test Conditions - Volume** | 50 ml |
| **Test Conditions - Temperature** | ambient |
| **Test Conditions - Time** | 2,000 hr |
| **Test Conditions** | Wash the membrane thoroughly in type 1 water before drying the membrane under vacuum at 50°C for 4 h. Measure the mass. |
| **Mass loss formula** | Mass loss (%) = $[(mass_{initial} - mass_{after})/mass_{initial}]x100$ |
| **Number of repeats (mass loss)** | 3 |
| **Area specific resistance (EoT)** | Measure conductivity as specified in 2.1.7.1 using ac-impedance. Determine variation in area specific resistance from the high frequency intercept. |
| **Data treatment** | Report percentage variation of ASR versus the BoT value |

| METRIC | Conditions | TARGET |
|---|---|---|
| **Mass Loss** | average of 3 readings of mass loss and ASR, and to 4d.p. | <5% over 2,000 h ageing test in KOH |

## Membrane Oxidative 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** | 4 cm x 4 cm |
| **Concentration of hydrogen peroxide** | 3% by weight |
| **Concentration of $Fe^{2+}$** | 4 ppm by weight |
| **Test Conditions - Volume** | 50 ml at pH=3 by addition of diluted HCl |
| **Test Conditions - Temperature** | 80°C |

| | | |
|---|---|---|
| **Test Conditions - Time** | 2 hr | |
| **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 (%) = $[(\text{mass}_{\text{initial}} - \text{mass}_{\text{after}})/\text{mass}_{\text{initial}}] \times 100$ | |
| **Number of repeats** | 3 | |
| **METRIC** | **Conditions** | **TARGET** |
| **Mass Loss** | average of 3 readings of mass loss to 4d.p. | No target for monitoring |

### 2.1.7.4 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** | 4 cm x 4 cm | |
| **Test conditions** | Immersed 24 hr in 50ml Type 1 water at 95°C<br>Dried in a vacuum oven at 50°C for 4hr<br>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 |

### 2.1.7.5 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±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 µm/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 | 30 µm |
| **Membrane Uniformity (µm)** | As required | ±10% of the mean thickness |

### 2.1.7.6 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 consisting of Pt/C gas diffusion electrodes 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<br>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 | 100 mV to 400 mV |
| Scan rate | 2mV/s |
| Test Method | • Assemble cell with membrane and Pt/C gas diffusion electrodes 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.<br>• Set the temperature and pressure as required<br>• Flow 100% humidified hydrogen on anode (equiv. of 1.5 stoich at 1 A/cm$^2$) and de-aerated water/KOH on cathode (5 ml/min) to keep membrane hydrated<br>• Sweep cathode potential from rest potential (100 mV) to 400 mV against anode at 2 mV/s<br>• Report crossover rate at 400 mV |

| METRIC | **FREQUENCY** | **TARGET** |
|---|---|---|
| Hydrogen crossover current | | <1 mA/cm$^2$ at ambient pressure |
| Hydrogen crossover rate | | <0.070 ml/min/cm$^2$ hydrogen |

### 2.1.7.7 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 and hydroxide uptake and linear expansion (swelling), $\lambda$, ion concentration

### Protocol and Metrics

| | |
|---|---|
| Pre-conditioning | The water and KOH uptakes are calculated by the difference in weight before and after the immersion of the dried samples in water or KOH 1 M solution at 30°C for 24 hrs.<br>Samples of the membrane should be dried in an oven to constant weight. Preferably, to reach the dry state, the samples were maintained in an oven under vacuum (1,000 mbar) for 2 hrs at 50°C. |
| Operating conditions: | |
| Measurement technique | A balance capable of measuring to 0.0001g.<br>Calipers capable of measuring 0.01mm |
| Membrane sample size | Approximately 20 mm x 10 mm. |
| Hydration temperature | 30°C, 60°C and 90°C |
| Technique | • A minimum of three samples should be used for each test.<br>• The size and weight of pre-conditioned samples are determined.<br>• The samples are then placed in containers of deionised water and placed in an oven at the appropriate temperature for 24 hours.<br>• After 24hrs, the samples are removed from the oven and measurements of length and weight are taken. |
| Analysis | • % Water Uptake = ((hydrated mass – dry mass) / dry mass)*100<br>• % Linear Expansion = ((hydrated length – dry length) / dry length)*100.<br>• The dimensional variation is calculated in the same operative conditions of water uptake on a rectangular sample, measuring the length (L) of the longest side.<br>• The swelling is calculated as the ratio $\Delta L/L$. $\lambda$ which is the number of water/KOH molecules per functional group, is calculated as the ratio between the uptake and the IEC. The reported values are an average of three different measurements.<br>The anion concentration, expressed in M, is calculated as follows: |

$[A^-]=IEC_{A^-}\ m_{dry}/V_{wet}$

Where:

$A^-$ is OH or Cl anion and the corresponding IEC (meq/g) is calculated by acid-base or Volhard method;

$m_{dry}$ is the dry mass of the sample expressed in g;

$V_{wet}$ is the wet volume, expressed in $cm^3$.

| METRIC | **FREQUENCY** | **TARGET** |
|---|---|---|
| Water Uptake | As required | No target |
| Linear Expansion | As required | dry/wet < 4% |

### 2.1.7.7 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 Tg | At maximum of tan(ä) | No target for monitoring |

### 2.1.7.7 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.<br>Width of narrow section = 6 mm<br>Length of narrow section = 33 mm<br>Gauge length = 25 mm<br>Distance between the tabs = 65 mm<br>Length overall = 115 mm<br>Radius of fillet = 14 mm<br>Outer radius = 25 mm |
| Initial Grip Separation | 60 mm |
| Initial Strain Rate | 0.5 mm/mm.min |
| Rate of Grip Separation | 30 mm/min (Rate of Grip Separation = Initial Strain Rate x Initial Grip Separation) |
| Load cell | Suitable for material tested |
| Water bath temperature | 23±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 | Mechanical<br>elongation at break >100% |
| Young’s Modulus (MPa to 3 significant figures) | As required | Modulus ~ 15 MPa. |

## 2.2 ELECTROCATALYSTS ASSESSMENT

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.

Electrocatalyst assessment is thus 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.

### 2.2.1 EX-SITU CATALYST ASSESSMENT

*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.

The protocols regard an identification of the main physico-chemical properties, such as bulk and surface composition, mean crystallite size, particle size, surface area, that influence predominantly the electrocatalytic activity.

### 2.2.2 ANIONE Catalysts Specifications and Procedures:

Specific details for the ANIONE Catalysts Specifications and Procedures are provided below with regard to some relevant catalysts assessment procedures that are of primary interest for electrolysis applications

*Summary of Procedures*

**Procedures**

| Number | Test |
|---|---|
| **1** | Chemical properties |
| **2** | Structural properties |
| **3** | Surface properties |

### 2.1.7.1 Catalysts physico-chemical properties

**Summary**

Anode and cathode are produced in powder form or milled to form a powder in order to allow ink preparation in combination with the ionomer for MEA fabrication.

## Chemical Properties

### Catalyst Composition

| | |
|---|---|
| **Elemental analysis** | Determine the chemical composition from X-ray fluorescence, ICP or EDX analysis and report the level of accuracy |
| **Light elements:** | Determine the content of light elements from CHSNO elemental analysis |
| **Cathode catalyst content on carbonaceous supports** | For the cathode determine the carbonaceous content from thermogravimetric analysis by burning the organic fraction at 950-1,000°C |

| METRIC | FREQUENCY | TARGET |
|---|---|---|
| Catalyst Composition at. or wt% | BoT and EoT | No target for monitoring |

## Structural and morphological properties

### Structure, solid solutions, crystallite size, particle size

| | |
|---|---|
| **Structure** | Carry X-ray diffraction (XRD) to determine crystallographic structure |
| **Solid solutions:** | Determine degree of formation of solid solutions from peak shift after calibration using Vergard's law |
| **Crystalline properties** | Determine mean crystallite size from peak broadening using the Debye-Scherrer method |
| **Morphological properties** | Determine mean particle size from TEM analysis |
| **Dispersion properties** | Determine particle size distribution from TEM analysis |
| **Total Surface area** | Determine overall surfaced area from BET analysis |

| METRIC | FREQUENCY | TARGET |
|---|---|---|
| Mean crystallite size anode and cathode catalyst | BoT and EoT | < 10 nm |
| Mean particle size anode and cathode catalyst | | <10 nm |
| Surface area anode and cathode catalyst | | >200 $m^2/g$ |

## Surface Properties

### Catalyst Composition

| | | |
|---|---|---|
| **Surface analysis** | Determine the oxidation state and the atomic concentrations of the elements on the surface from X-ray photoelectron spectroscopy -XPS<br>• Repeat XPS measurements after successive 5 kV Ar+ ions sputtering to determine bulk composition<br>• Carry out chemical profile analysis of catalyst particles using combination of LEISS and XPS | |
| **METRIC** | **FREQUENCY** | **TARGET** |
| Catalyst Composition at. % | BoT and EoT | No target for monitoring |

### 2.2.3 IN-SITU CATALYST ASSESSMENT (Half-cell and single cell)

Experiments, serving as a screening tool to compare the electrochemical degradation in an acidic environment of different catalysts are identified. For these experiments, the selected electrolyte is 1 M KOH and the temperature range varies from ambient temperature to 90°C in steps of 10°C. Reference temperature is fixed at 50°C.

Screening of catalysts is carried out at both half-cell and single cell level in the presence of the 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 reference electrode (DHE or RHE). 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 0.1 M, 1 M KOH for operation in a liquid electrolyte half-cell and FUMATECH (Fumasep FAA-3-50) membrane in combination with Fumasep FAA-3-50 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.

Catalyst assessment in MEAs: this will be carried out to evaluate the electrochemical behaviour, preferably in a wide range of temperatures (R.T. to 90°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 50°C will be carried out to analyse the catalyst properties in relation to warm-up characteristics of the practical device.

#### *2.2.2.1 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 alkaline environment and electrocatalytic activity. The reference temperature for half-cell testing will be 50°C. The reference electrode is Hg/HgO.
The baseline anodes consist of a GDL type Ni-based diffusion layer coated with a catalytic layer containing 2-3 mg $cm^{-2}$ of catalyst loading with 33% wt. ionomer. The baseline cathodes are based on a GDL type Ni-based diffusion layer or carbon paper/cloth gas diffusion backing layer coated with 2-3 mg $cm^{-2}$ of catalyst loading with 33% wt. ionomer.
Pre-screening is carried out in liquid electrolyte by half-cell galvanostatic polarization measurements for hydrogen and oxygen evolution in KOH (0.1 M or 1 M) by using electrodes similar to those developed for single cell testing.
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] |
|---|---|
| 0.0002 | |
| 0.0005 | |
| 0.001 | |
| 0.002 | |
| 0.005 | |
| 0.01 | |
| 0.02 | |
| 0.03 | |
| 0.04 | |
| 0.05 | |
| 0.06 | |
| 0.08 | |
| 0.1 | |
| 0.12 | |
| 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 | |

The cut-off voltage is fixed at 2.2 V RHE for the anode and -1.0 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 potentostatic 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 0-1.4 V RHE to get information of the electrochemical properties and to study the specific degradation oxidation/ process that may occur under unusual conditions. To determine the anode surface area the selected range varies from 0.4 to 1.4 V RHE to avoid relevant metal catalyst oxide reduction at low potentials. The sweep rate is

selected in the range 20-150 mV $s^{-1}$. Assessment of ECSA for the anode is made by integration of specific charge q* 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/$cm^2$ is calculated from AC-impedance, preferably at OCV, 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 (or preferably 0.4-1.4 V RHE for the anode) where no faradaic reactions occur regarding water splitting. If the CV experiments are carried out in single cell, water/KOH solution is supplied to both cathode and 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. However, this approach can be used 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. Potential holding at -0.5 V vs. RHE for 48 h will be used to test the eventual degradation of the cathode properties in a three-electrode configuration mode. Reference cyclic voltammetry to investigate ECSA loss will be carried out

To assess degradation, pre- and post-operation physico-chemical analyses will be carried out by XRD (structural), XRF (elemental), TEM and SEM-EDX (morphological), XPS (surface analysis).

#### *2.2.2.2 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 a Pt/C cathode which acts both as reference and counter electrode (RHE, assuming modest polarization). Alternatively, humidified nitrogen can be fed to the cathode to allow for hydrogen evolution under operation and this will form a dynamic reference electrode (DHE).

In single cell testing of anode catalysts, 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 large (1 mg $cm^{-2}$) 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 in the hydrogen pumping mode with the counter/reference electrode fed with humidified hydrogen and acting as anode. This should contain large Pt loading as reported above to avoid significant reference electrode polarization and the cathode under investigation fed with demineralised water.

Protocols for anode and cathode polarization curves regard the galvanostatic operation mode as reported above.

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.

*Electrochemical diagnostics for in-situ catalyst assessment:*

In situ catalyst assessment by 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 – 200 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. The polarisation resistance associated to catalyst behaviour is determined at low current density/ low cell potential from the difference between the low frequency and high frequency resistance.

Cyclic voltammetry for the anode is carried out as specified for the half-cell measurement by feeding humidified $H_2$ at the cathode (flow rate 100 ml $min^{-1}$) and using Pt/C reference/counter electrode (RHE or DHE). 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 $H_2$ at the anode compartment (flow rate 100 ml $min^{-1}$) and using Pt/C reference/counter electrode (RHE or DHE). The dew-point temperature is equal to cell temperature. The Pt/$H_2$ interface acts both as reference (RHE) and counter electrode. Determination of the coulombic charge is reported above for the half-cell. Assessment of surface area from the capacitance values should be preferably carried out in half-cell but the in-situ measurements can provide information on the interface with the electrolyte.

Accelerated stress tests for both the anode and cathode is made through a high potential hold test i.e. 100 hrs cell potential hold at 2.2 V at relevant temperature and pressure operation conditions. Water/KOH feed, temperature and pressure as above. This is followed by physico-chemical analysis.

### 2.2.4 Baseline (benchmark) catalysts:

CENmat HYDROGEN EVOLUTION Mo-carbide and OXYGEN EVOLUTION NiFe-oxide catalysts have been indentified as benchmarks. Catalysts are supplied as powders with recommendations for ink preparation.

Or

NiCo-spinel from C-Tech Innovation and MMO from C-Tech

### 2.2.5 Dataset for catalysts

Electrocatalyst performance evaluation:
-anode overpotential (Ea) measured at 1 A $cm^{-2}$ under relevant temperature and pressure conditions from IR-free Tafel plots in the presence of a specific catalyst loading (> 2-3 mg active catalyst $cm^{-2}$). For in-situ measurements, a Pt/C cathode as reference/counter-electrode can be used (DHE or RHE).
-cathode overpotential (Ec) measured at 1 A $cm^{-2}$ from the IR-free cathode polarization curve. For in-situ measurements, the hydro pump method can be used Pt/C as reference/counter-electrode (DHE or RHE).

## 2.3 MEA ASSESSMENT IN SINGLE CELL

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.

It is the aim of the Consortium to use the same cell for MEA assessment in single cell. The most appropriate single cell set-up will be identified during the project. 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 $cm^2$, 8 $cm^2$, 25 $cm^2$ , 100 $cm^2$ etc. will be used. Scale-up studies will concern sizes ≥100 $cm^2$.

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.

Membrane characterisation in MEAs 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 ($H_2$).

Catalyst testing in MEAs will be carried out to evaluate the electrochemical behaviour, preferably in a wide range of temperatures (RT 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 analyse the catalyst properties in relation to warm-up characteristics of the practical device.

### 2.3.1 Harmonised MEA assessment in single cell

The MEA assessment procedure was agreed among three H2020 FCH JU projects i.e., ANIONE, CHANNEL AND NEWLY and is reported below.

## 2.4 SPECIFICATION OF PERFORMANCE, DURABILITY, CYCLE OPERATION OF AN AEM ELECTROLYSIS SINGLE CELL

### 2.4.1 Assessment MEA performance in single cell

MEA assessment is first carried out in a small single cell (≤25 $cm^2$ geometrical area) and thereafter the optimised MEA is assessed in large area cells (>25 $cm^2$). Cell compression and leak tests should be carried out according to the usual practise. In the case of asymmetric electrodes, current should be normalised by the largest electrode area.

The flow field design can vary substantially for the different laboratories. This of course can affect MEA performance. However, for comparison a standard design should be identified.

*Reference temperature* for MEA assessing is 50°C, the *temperature range* vary from 30°C to 90°C in 10°C increments. In specific cases, results can be provided until the maximum achievable temperature. It will be specified if this is due to the membrane or to the test stand.

In ANIONE, the aim is to operate the AEM electrolyser with almost pure water. The approach is to start from diluted KOH solution feed and move progressively towards pure water. However, we do not exclude to reach a possible trade-off. The motivation is determined by the fact that beside durability, the achieving of high efficiency is prioritized in this project. Thus, operating conditions are optimised to maximise efficiency and durability.

In PEM electrolysis, the use of ultrapure water feed is mandatory to achieve high efficiency. Instead, for AEM electrolysis, it may be avoided feeding ultrapure water in favour of a diluted KOH solution to maximise efficiency while achieving good stability and avoiding the complex management of caustic solutions as well as the extreme water purification.

In this regard, it is suggested assessing the AEM electrolyser for operation under three different conditions feed conditions i.e. pure water feed, 0.2 M KOH and 1 M KOH.

For pure water, conductivity should be monitored at the cell inlet. Water must be purged with nitrogen (5N). This can be done at the water/solution refill tank. The recirculating solution pH should be monitored especially during durability operation. Alternatively, this can be checked at regular intervals.

*Reference water or supporting electrolyte feed rate* at the cell is fixed to 1 g $cm^{-2}_{cell\ area}$ $min^{-1}$. Since the gravimetric density for water and diluted KOH is close to 1 g $ml^{-1}$, the feed rate can be fixed at 1 ml $cm^{-2}$ $min^{-1}$. . For pure water operation: *Water quality*: $\rho >$ 5 MOhm cm.

This as long as the temperature difference between in-let and out-let of the electrolyser does not go above 5ºC. Alternatively, recirculating water/solution flow rate can be increased to 2 g $cm^{-2}$ $min^{-1}$ to keep temperature gradient ($T_{outlet}$-$T_{inlet}$) within 5°C.

The water/solution can be fed either to both electrode compartments (same flow as indicated) or to a single electrode. This must be reported. Reference operation includes water/solution feed to both compartments.

*Differential pressure or balanced pressure can be selected*. This must be reported. Reference cathode pressures (gauge) are: 0 $bar_{rel}$ for low pressure studies, $15_{rel}$ and 30 $bar_{rel}$ for high pressure experiments (maximum deviation: 0.2 bar).

Considering that in some projects high pressure operation is planned only at stack level, if there are no alternative options, single polarisations curves can be carried out at ambient pressure only. However, it is recommended to make efforts to carry out single cell tests and determination of hydrogen concentration at the anode under pressurised mode too to allow for a comparison under real operating conditions.

*MEA conditioning*: MEA is installed in a single cell and equilibrated at the operating temperature with deionised water ($\rho$>5 MOhm cm) or supporting electrolyte solution. This is carried out at ambient pressure, with water/solution pre-heated to the operating temperature at a flow rate of 1 g $cm^{-2}$ $min^{-1}$.

Conditioning is continued with an applied load of 0.05 $A.cm^{-2}$ for 24 hours for pure water/KOH operation alternatively a conditioning procedure at 0.2 A $cm^{-2}$ for 2 h should be adopted when KOH solution is fed to the cell. This to favour membrane hydration, in-situ purification and stabilisation of the anode and cathode catalysts oxidation state.

*Load switch:* OCV time interval between conditioning and polarisation curves should be kept to 30 s.

*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. Reproducibility must be checked by at least two repetitions. In the case of significant deviation (exceeding ±5 mV), error bars should be reported.

*Sweep mode:* at ambient pressure, for an initial assessment, the polarization curve is measured from lowest to the highest current density (ascending part of the polarisation curve) followed by a measurement in reverse order that is from highest to lowest current density (descending part of the polarisation curve). This will allow assessing the maximum operating current density.
Once the maximum operating current density for the specific MEA is established and for operation at high pressure, the performance is instead measured from the highest to the lowest current density (descending part of the polarisation curve) followed by a measurement in reverse order (ascending part of the polarisation curve).

*Safety:* The operating pressure is stabilized at the maximum current density before carrying out the polarization curve in descending mode until the minimum partial load. The $H_2$ concentration in the $O_2$ stream should be monitored at each current density to avoid reaching the flammability limit (4% $H_2$ in $O_2$).

*Cut-off-voltage:* The measurement should be aborted when the cell voltage is 2.0 V or above (cut-off voltage). However, if a project target is regarding the achievement of specific current densities at a cell voltage of 2 V, a cut-off voltage of 2.1 or 2.2 V can be selected as alternative.

*Data collection:* Variation of the current density is thus carried out in steps as reported below; the duration of each step (dwell time) is 1 min (pseudo steady state-condition). The average potential is reported at each current density in a table such as the one reported below.
The left-hand column (blue colour) matches exactly with the sampling dataset reported in the "EU Harmonised Polarisation Curve Test Method for Low Temperature Water Electrolysis" released by JRC.
The isothermal condition (no relevant temperature gradient at different current densities) could be established by using a thermostat for the water/solution recirculating. Water/solution recirculation thus acts as a thermostating fluid. The cell temperature and pressure should be stabilised at the maximum operating current density before proceeding with the polarisation curve from the maximum current density to the open circuit voltage. In any case, the inlet water temperature must be controlled; this is used as the reference point.
Low current density measurements and logarithm-type current sampling can be useful in the case it is needed to determine the Tafel slope. Otherwise, the polarisation can start at 0.01 A $cm^{-2}$.

| Current Density<br>[A·cm$^{-2}$] | Cell Voltage<br>[V] |
|---|---|
| 0.0002 | |
| 0.0005 | |
| 0.001 | |
| 0.002 | |
| 0.005 | |
| 0.01 | |
| 0.02 | |
| 0.03 | |
| 0.04 | |
| 0.05 | |
| 0.06 | |
| 0.08 | |
| 0.1 | |
| 0.12 | |
| 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 | |

## Assessment of MEA performance

| Single cell polarisation curve | MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks |
|---|---|
| Test Method:<br>*Single cell performance assessment* | • Feed cell with water/solution at a rate of 1 ml/min/cm$^2$<br>• Set thermostat to the desired temperature<br>• Cell conditioning: apply a load of 0.05 A cm$^{-2}$ for 24 hours or 0.2 A cm$^{-2}$ for 2 hours depending on the feeding mode to favour membrane hydration, in-situ purification and stabilisation of the anode catalyst oxidation state.<br>• Fix cut-off voltage to 2.0 V, according to the selected current density range.<br>• Carry ac-impedance analysis (galvanostatic or potentiostatic) <u>Galvanostatic:</u> fixed current density of 0.2 and 1 A cm$^{-2}$, from 100 kHz to 100 mHz with an amplitude of 5% pk-pk of the applied current (Reference test).<br><u>Only for further diagnostic purposes:</u> Potentiostatic: 1.5 V and 1.8 V. from 100 kHz to 100 mHz. 10 mV rms oscillation.<br>• Stabilize the selected pressure (cathode differential pressure or balanced pressure) and temperature at the maximum current density. Use a thermostat to manage for isothermal operation in combination with maximum current density.<br>• Carry out the polarisation curve as defined above in descending mode after stabilising outlet water temperature at the maximum current density<br>• Monitor $H_2$ concentration in oxygen at each current density<br>• Decrease pressure at low current densities if needed ($H_2$ in $O_2$ >3%)<br>• Eventually, monitor $O_2$ concentration in hydrogen.<br>• Repeat polarisation curve in ascending mode to check for hysteresis.<br>• Repeat tests at various temperatures (30-90°C) and pressures (ambient to 30 bar).<br>• Report data as Potential (V) vs. Current density (A cm$^{-2}$) along with temperature, pressure and catalysts loadings, feed mode. The reported cell temperature is the water/solution temperature at cell outlet. |

### 2.4.2 Assessment of MEA stability in single cell

***Steady state operation:***
Assessment of MEA stability

| | |
|---|---|
| Single cell durability study | MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks |
| Test Method:<br>*Single cell assessment* | • Safety conditions as reported for the polarisation curve.<br>• Feed cell with water/solution at a rate of 1 ml/min/cm$^2$<br>• Solution replacement every 14 days (unless this is required earlier for specific reasons). Deviation from the protocol should be annotated and reported.<br>• Set thermostat to desired temperature<br>• Cell conditioning: apply a load of 0.05 A cm$^{-2}$ for 24 hours or 0.2 A cm$^{-2}$ for 2 hours depending on the feeding mode at ambient pressure<br>• Fix cut-off voltage to 2.0 V, according to the selected current density range<br>• Carry ac-impedance analysis (galvanostatic or potentiostatic) Galvanostatic: fixed current density of 0.2 and 1 A cm$^{-2}$, from 100 kHz to 100 mHz with an amplitude of 5% pK-pK of the applied current. Only for further diagnostic purposes: Potentiostatic: 1.8 V and 1.5 V. from 100 kHz to 100 mHz. 10 mV rms oscillation.<br>• Stabilize the selected pressure (cathode differential pressure or balanced pressure) and temperature at the selected current density.<br>• Carry out the BoT polarisation curve as defined above in descending mode and eventually other diagnostics<br>• Monitor $H_2$ concentration and decrease pressure at low current densities if needed (if $H_2$ in $O_2$ >3%).<br>• Eventually, monitor $O_2$ concentration in hydrogen.<br>• Carry out a durability test of 2,000 h at the selected current density (nominal 1 A cm$^{-2}$)<br>• Make electrochemical diagnostics (impedance and polarisation) every 100 hrs *whenever possible*. Keep operation at OCV fixed i.e. *15* min interval between each diagnostic test and restart the durability test.<br>• Carry out EoT polarisation, and eventually other diagnostics<br>• Report data as Potential (V) vs. Time (h) along with current density, temperature, pressure, catalysts loadings and feed mode.<br>• Determine average voltage increase from best fitting procedure (as indicated below). The approach is discussed below to deconvolute recoverable losses from the overall degradation. A linear fitting is suggested excluding the first |

| | |
|---|---|
| | 100 h and taking data points at the end of each continuous 400 hrs step in a durability test (see below).<br>- Determine performance and overall efficiency decrease at the nominal current density. Overall efficiency is the product of voltage efficiency and faradaic efficiency (under exothermic mode operation).<br><br>Efficiency is determined according to:<br>G. Tsotridis, A. Pilenga in "EU harmonised terminology for low temperature water electrolysis for energy storage applications", Publications Office of the European Union Publisher, ISBN: 978-92-79-90387-8 (online), 978-92-79-90388-5 (print). |

### 2.4.3 Assessment of MEA dynamic behaviour

***Cycled operation:***

Assessment of MEA dynamic behaviour:

| | |
|---|---|
| Single cell dynamic performance study | MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks |
| Test Method:<br>Single cell assessment of the dynamic behaviour | • Safety conditions as reported for the polarisation curve.<br>• Feed cell with water at a rate of 1 ml/min/cm$^2$<br>• Set thermostat to desired temperature<br>• This experiment is carried out at ambient pressure<br>• Fix cut-off voltage to 2.0 V<br>• Apply cell conditioning as above<br>• Carry out the BoT polarisation curve, monitor $H_2$ concentration in $O_2$<br>• Apply a load of 1 A cm$^{-2}$ (or the selected nominal current) for 100 hours at ambient pressure<br>• Followed by a 2 step cycle:<br>- Step 1: 18 seconds at 0.2 A/cm$^2$ (or the selected nominal current corresponding to 20% load)<br>- Step 2: 18 seconds at 1 A/cm$^2$ (or the selected nominal current corresponding to 100% load)<br>- Repeat this cycle 10,000 times to form a first set of accelerated stress test - AST (corresponding to ~100 h)<br>• Carry out control polarisation and eventually other diagnostics<br>• Repeat Steady-state and AST to complete 5 sets totalling 1,000 hrs with 5 diagnostic intervals<br>• Carry out EoT polarisation, and eventually other diagnostics<br>• Report data as Potential (V) vs. Time (h) along with current density, temperature, pressure, feed mode and catalysts loadings.<br>• Determine average voltage increase from best fitting procedure<br>• Compare polarisation curves, ac-impedance spectra and EoT CV with those recorded on the same cell or a similar cell at the BoT.<br>• Determine performance and efficiency decrease at the nominal current density, surface area, series and polarisation resistance changes |

### 2.4.4 Assessment of gas crossover through the membrane during MEA testing

***Gas crossover:***
Assessment of gas crossover through the membrane during MEA operation

| | |
|---|---|
| Gas crossover study | MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks |
| Test Method:<br>*Single cell assessment* | • Safety conditions as reported for the polarisation curve.<br>• Feed cell with water/solution at a rate of 1 ml/min/cm$^2$<br>• Set thermostat to desired temperature<br>• Cell conditioning: apply a load of 0.05 A cm$^{-2}$ for 24 hours or 0.2 A cm$^{-2}$ for 2 hours depending on the feeding mode at ambient pressure<br>• Fix cut-off voltage to 2.0 V, according to the selected current density range<br>• Under galvanostatic operation fix the current density at 1 A cm$^{-2}$ and pressurize the cell (differential or balanced pressure).<br>• Stabilize the selected pressure (cathode differential pressure or balanced pressure) and temperature at the selected current density.<br>• Measure the $H_2$ concentration in the dry $O_2$ stream at the anode by a gas sensor or microGC by first passing the anodic stream through a condenser and a drying bed.<br>• Eventually repeat the same experiment for the cathode.<br>• Monitor $H_2$ concentration after sufficient time to achieve equilibration<br>• Repeat the measurement of $H_2$ in $O_2$ until achieving constant value (±5% deviation)<br>• Decrease current density while monitoring $H_2$ concentration<br>• At current densities of 0.7, 0.5, 0.3, 0.2, 0.1 A cm$^{-2}$ repeat the measurement of $H_2$ in $O_2$ until achieving constant value (±5% deviation) at each current.<br>• Decrease pressure at low current densities if needed (if $H_2$ in $O_2$ >3%).<br>• Eventually, repeat the same experiment at the anode i.e. monitor $O_2$ concentration in hydrogen.<br>• Report data as vol% $H_2$ in $O_2$ vs. current density at specific pressure and temperature. |

| **METRIC** | **FREQUENCY** | **TARGET** |
|---|---|---|
| $H_2$ in $O_2$ (and possibly $O_2$ in $H_2$) vs. current density at specific pressure and temperature. | At the indicated current densities of 1, 0.7, 0.5, 0.3, 0.2, 0.1 A cm$^{-2}$ (if $H_2$ in $O_2$ < 3%) in descending mode | < 1 vol. % $H_2$ in the $O_2$ stream at the anode at nominal current density |

### 2.4.5 Assessment of the increase of membrane area specific resistance during MEA operation

***Increase of membrane area specific resistance:***
Assessment of the area specific resistance variation for the membrane during electrolysis operation

| | |
|---|---|
| Area specific resistance | MEA assembling according to the project fabrication procedures. Installation of the MEAs in single cell with related checks |
| Test Method:<br>*Single cell assessment* | • Carry out the experiment as defined in 2.4.2<br>• At BoT and EoT, determine ASR from the high frequency resistance according to the ac-impedance results at high current densities.<br>• Determine the percentage variation of ASR during 2,000 hrs electrolysis operation<br>• Report data as % increase of ASR at specific current density, pressure and temperature. |

| **METRIC** | **FREQUENCY** | **TARGET** |
|---|---|---|
| BoT and EoT | BoT and EoT | Area specific resistance (ASR) increase lower than 5% in 2,000 h electrolysis operation. |

### 2.4.6 DETERMINATION OF THE DEGRADATION RATE IN DURABILITY STUDIES

Reversible losses are usually recorded when the cells/stacks are operated at high current densities and several start-up/shutdown cycles are eventually occurring in durability studies.

During a durability test of 2,000 hrs, some unavoidable test interruptions may occur requiring shutdown/start-up cycles. Thus, the number of cycles cannot be fixed.

Recoverable losses may be minimised by low operating current density and proper cell/stack design including diffusion layers/PTLs etc.

Some start-up/shutdown cycles can be also made on a voluntary basis with relative diagnostics to monitor the evolution of some relevant parameters using polarisation and impedance analyses. This will also avoid that for some unexpected reason one may lose some end of test analysis after 2,000 hrs without having any intermediate results.

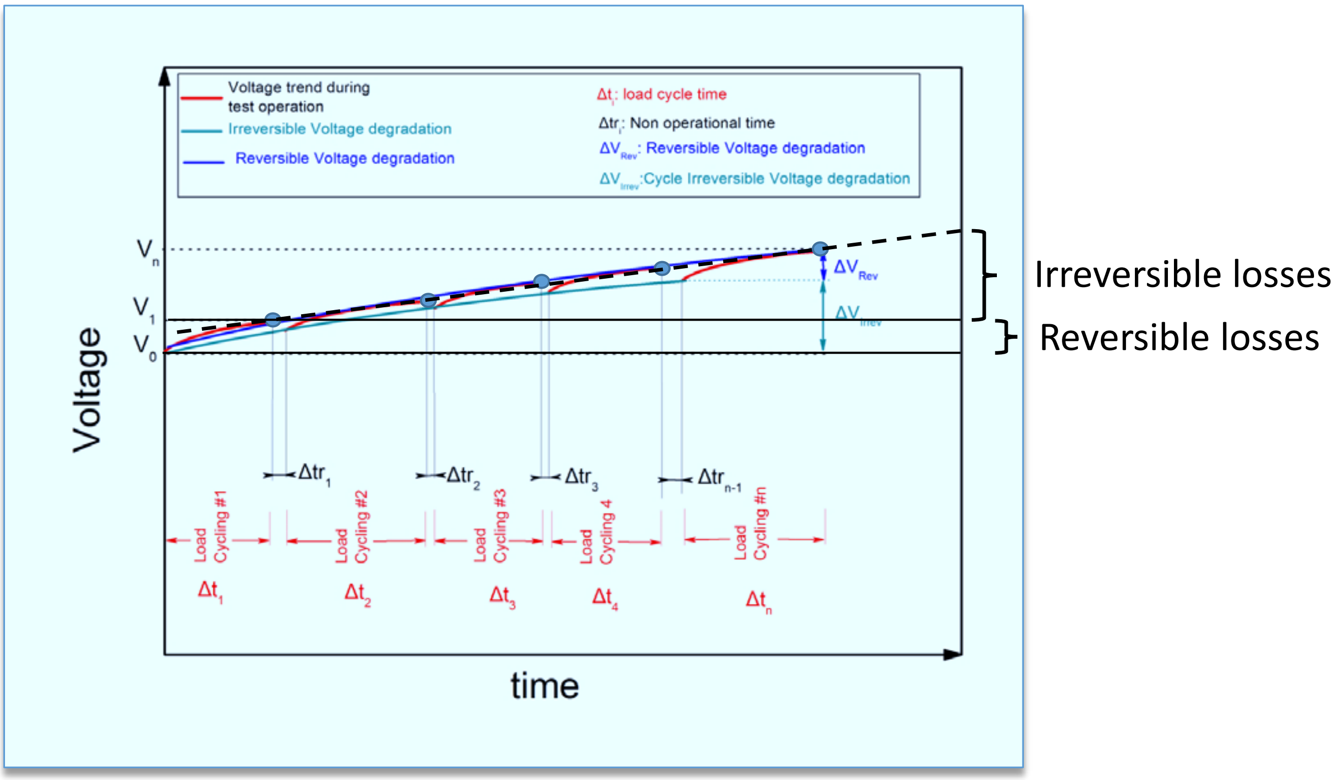
The method for determining reversible and irreversible losses is described below. In electrolysis, it is better to make reference to the end points after each operating step, just before shutdown, than to the initial points just after start-up.

The reason is that the duration of the rest interval at OCV, e.g. 1 h or 1 day may affect the initial points after each start up.

Rest interval may be fixed but there always some uncertainty associated with unexpected interruptions.

The endpoints of each step can be used for the linear fitting, provided that each step is larger than 400 h to minimise the recoverable losses effects occurring during start-up. It is pointed out that right now the JRC-IET approach for estimating degradation in low temperature electrolysis systems make use in the fitting of the initial points of each step and not the end-points. This is under discussion and it may be changed in the final release of the JRC-IET harmonisation document. However, if needed to compare results among stakeholders, one may use both methods (see figure below) and clearly specify the approach used.

The best fitting procedure is thus shown below in comparison to the JRC-IET approach.
It is suggested to perform linear fit of the end points of each step before the shutdown processes (excluding start-up points). The points are selected provided that each operating step is at least of 400 h to minimise recoverable losses during start-up effects.



### 2.4.7 Dataset for MEAs

MEA performance evaluation:
-cell potential is determined at 1 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 of the steady state test at 1 A cm$^{-2}$ as discussed above. Degradation rate reported in µV/h.

# 3 Stack assessment

Characterisation and test protocols for the assessment of performance, efficiency and durability of an AEM water electrolysis stack are defined in this section. The final stack developed in Anione will be tested inside a system which acts as a test station.
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). Constant current load operation and dynamic operation mode are assessed.
Stack durability studies may be accompanied by ex-situ tests to investigate degradation phenomena.

Protocols for non-active components such as diffusion layers and porous transport layers are also discussed in this section.

The procedures discussed in this section are summarized below:

1) *Protocols for the assessment of non-active stack components:*

   These mainly concern with diffusion layers, porous transport layers, bipolar plates, backing layers and current collectors that can be potentially used in the AEM electrolyser stack housing. Essentially, these consist in measuring variation in contact resistance before and after testing.

2) *Protocols for initial stack assessment*

   These are similar to the MEA testing protocols described above and concern with polarization and durability tests. Durability is assessed by investigation of voltage increase at constant current operation under specific conditions of temperature and pressure. The increase of mean cell voltage at specific current densities is thus used to assess performance loss. The stacks are initially assessed under stationary conditions.

3) *Protocols addressing the stack dynamic behaviour*

   These procedures are aiming to investigate the capability of the stack to sustain start-up / shutdown and load cycles. 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, analysis of recirculating water/solution and determination of the relative gas concentrations in the outlet streams. Post-operation physico-chemical analysis of the active components may be eventually performed in the case of relevant issues.

## 3.1 PROTOCOLS FOR ASSESSMENT OF STACK HOUSING COMPONENTS

The stack consists of MEAs, bipolar plates, diffusion or porous transport layers, sealing gaskets etc. These materials are not directly involved in the primary electrochemical process. However, they play a relevant role in determining stack performance and stability since distribute electrical energy and reactant over the active parts and collect reaction products. According to the specific role played inside the stack, their selection is made on the basis of relevant properties such as mechanical stability, conductivity, chemical stability, porosity (full density or porous transport layers) and capability to achieve proper sealing for pressurized operation.

Screening activities are essentially addressed to determine such properties and make use of various instrumentation. Post-operation physico-chemical analysis of non-active stack components are carried out to investigate degradation effects related with operation under practical conditions.

The electrical resistance of a porous metal layer increases by increasing its porosity; however, a higher porosity promote favour the escape of evolved gases. Identification of critical porosity (maximum achievable porosity) versus electrical conductivity in sintered metal fibres or metal foams is extremely important. Sintered metal fibres or powders with porosity lower than 50% can act as support for the active components in high-pressure water electrolysis due to their strong mechanical properties. Although these are compressed during the stack assembling procedure their porosity characteristics are not much altered. Metal fibres characterized by porosities higher than 50% can be used to favour gas removal and to enhance conductivity. Their combination can provide a graded porosity combining high gas transport, good conductivity and proper mechanical support. Gaskets allow to achieve proper sealing under pressurized conditions.
Thus, the main approach is to determine conductivity versus porosity and estimate accordingly the expected ohmic and mass transfer losses eventually using modelling analysis.

### 3.1.1 Physico-chemical characterisation of non-active stack components

Pre- and post-operation physico-chemical analyses of non-active stack components regard elemental (XRF), structure (grazing angle XRD), microchemical and morphological (SEM-EDX), surface (XPS) analysis of bare, altered or corroded parts.

Porosity can be measured by a variety of methods such mercury intrusion porosimetry, scanning electron microscopy imaging and by experimental set-up based on Archimedes' principle using a combination of fluids. Detailed analysis of porosity characteristics (e.g. pore radii distribution) can be carried out by using 3D X-ray microtomography (μ XCT). SEM analysis can allow to determine distribution of porosity in porous transport layer especially in the case of pore-graded gas diffusion layers.

Through plane and in-plane conductivity measurements can be carried out using the conventional procedures.

Mechanical properties of seals are investigated with methods similar to those above discussed for membranes and their arrangement with metallic components is studied by leak tests under pressure significantly higher than that used during normal operation.

The procedures for these physico-chemical analyses are the conventional ones; thus, such protocols have not been detailed here.

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. Conductivity test protocols are defined in the following.

### 3.1.2 Measurement of in-Plane Electrical Conductivity of non-active stack components

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**<br>**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** | • Plot each result in standard Nyquist form<br>• Where the signal first crosses the real axis, this is the series resistance (high frequency resistance)<br>• Contact resistance is ½ 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** |
|---|---|---|
| ***Nyquist plot*** | BoT, EoT | |
| ***Electronic conductivity*** | 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 a stack of 10-cells with about 100 cm$^2$ per cell active area.
The nominal rated hydrogen production capacity is planned in 0.4 Nm$^3$/h.
Stack testing is carried out under controlled conditions in designed system operating at specific temperatures and pressures.

### 3.2.1 Stack performance assessment from Current-Voltage Polarization Curve

This is a measure of the stack voltage as a function of the applied current. 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 kWh/ kg $H_2$ and efficiency is referred to the HHV of $H_2$; beside this, the average cell voltage at a specific current density of 1 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<br>Protocol and Metrics | |
|---|---|
| **Pre-conditioning** | Stack MEAs must be equilibrated with water (hydrated) or with diluted KOH (0.2- 1 M) prior to measurement.<br>Before carrying out polarization measurements, it is recommended to run the stack at low current density (0.05 A cm$^{-2}$) for at least 24 hours to ensure the MEAs are properly conditioned |
| **Operating conditions:** | |
| **Control** | Galvanostatic (current controlled; voltage recorded); cut-off voltage of 2.2 V/cell |
| **Cell size/number of cells/ series connection** | As appropriate 10 cells, 100 cm$^2$ |
| **Water/solution temperature** | Recorded on both exits and reported with I-V curve |
| **Pressure** | In the first trial, 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 1.0 A·cm$^{-2}$ |
| **Procedure** | i) Carry out the first polarization curve in ascending mode at ambient pressure to determine the maximum current density achievable before reaching the cut-off voltage. In any case, do not increase current density above 1 A cm$^{-2}$.<br>ii) At the maximum achievable current or at 1 A cm$^{-2}$ pressurize the system.<br>iii) Repeat the polarization curve in descending mode under pressure until the minimum partial load (conc. $H_2$ in $O_2 \leq 3\%$ vol.), thereafter decrease the pressure to ambient pressure and continue the test until reaching the lowest current of 2 mA·cm$^{-2}$.<br>iv) Repeat tests i) - iii) to confirm reproducibility (two repetitions) |

| | |
|---|---|
| **Step size** | Logarithm sampling: Smaller step size 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 (group of cells) voltage |
| **Technique** | • Hold current at 100 mA·cm$^{-2}$ for 5 minutes before polarisation to ensure catalysts are in the correct oxidation state<br>• Step current to 2 mA·cm$^{-2}$ carry the first polarisation and proceed as specified in ii)-iv).<br>• 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)<br>• 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)** | | ≤50 kWh/kg $H_2$ at $H_2$ production rate of ≥4 Nm$^3$ /h (0.036 kg $H_2$/h). |
| **Efficiency (pseudo steady state test)** | | ~ 80 % vs. HHV of $H_2$ at 1 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, $\dot{n}_{H2}$ expressed in moles per hour multiplied by the HHV expressed in Wh per mole and divided by the electrical DC power supplied, $P_{DC}$ expressed in Watt.

$$\eta^{HHV}{}_{stack}\% = [(HHV_{H2} \cdot \dot{n}_{H2}) / P_{DC,\,stack}] \cdot 100$$

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]** |
|---|---|---|
| 0.002 | | |
| 0.005 | | |
| 0.01 | | |
| 0.015 | | |
| 0.02 | | |
| 0.05 | | |
| 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 | | |
| 1.0 | | |

Note: recirculated water/solution temperature and gas pressures should be controlled and recorded.

The polarisation curve is carried out on a stack of 10 cells, ~100 cm$^2$ area. The average cell potential at a fixed current densities of 1 A cm$^{-2}$ is determined from the polarisation curves and reported.

### 3.2.2 Stack durability assessment under stationary conditions

The stack stability assessment under stationary conditions consists in a Stack steady-State Test of 2,000 hrs at 1.0 A/$cm^2$ and the determination of the stack voltage and efficiency at the nominal capacity. Efficiency losses are reported as µV/h and %/yr.

Stack is tested under constant load, temperature and pressure, to measure the decay rate at 1 A/$cm^2$.

| Stack steady-State Test at 1 A/$cm^2$<br>Protocol and Metrics | |
|---|---|
| **Stack Conditioning** | Refer to preconditioning above reported |
| **Test Conditions** | Short-stack or Stack of nominal capacity<br>1. Before starting test, operate for 24 hrs at steady-state, 0.05 A/$cm^2$ for conditioning.<br>2. Measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Curve Procedure (Current Range: 2 mA/$cm^2$ – 1 A/$cm^2$).<br>3. Operate the stack at a steady-state 1.0 A/$cm^2$.<br>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/$cm^2$ – 1 A/$cm^2$). |
| **Total Time** | 2,000 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 |
|---|---|---|
| **Monitor pH and analyse metallic ions release in the recirculating water/solution.** | Continuously or every 100 hrs of steady-state operation from the beginning of the test. | No target for monitoring |
| **Monitor conductivity the recirculating water/solution** | Continuously or every 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 3% $H_2$ in $O_2$ | $H_2$ concentration in the oxygen stream <1 vol.% at specific pressure and current |
| **Voltage Degradation** | 2,000 hrs of operation after first I-V curve. | ≤ 6 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 after drying** | Every 100 hrs | ≥ 0.4 $Nm^3$/h |
| **Energy consumption or** | | ≤50 kWh/kg $H_2$ at $H_2$ production rate of ≥4 $Nm^3$ /h (0.036 kg $H_2$/h). |
| **Efficiency** | | ~ 80 % vs. HHV of $H_2$ at 1 A $cm^{-2}$ current density |

The time-test curve is carried out on a stack of 10 cells of 100 $cm^2$ area at a fixed current densities of 1 A $cm^{-2}$. Degradation in average cell potential is determined from a 2,000 hrs time-test using line of best fit and excluding the first 100 hrs of conditioning and reported.

## 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 dynamic conditions such as load cycles 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.

| Stack Cycling Test Protocol and Metrics | | |
|---|---|---|
| **Stack Conditioning** | Refer to stack conditioning procedure above reported | |
| **Test Conditions** | Stack of nominal capacity; ambient pressure; reference temperature<br>1. Before starting test operate for 24 hrs at steady-state, 0.05 A/$cm^2$.<br>2. Measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Polarisation Curve Procedure (Current Range: 2 mA/$cm^2$ – 1 A/$cm^2$; cut-off voltage 2.2 V/cell).<br>3. Followed by a 2 or 3 step cycle:<br>● Step 1: 10 seconds at 0.1 A/$cm^2$ (10% load)<br>● Step 2: 10 seconds at 1 A/$cm^2$ (100% load)<br>● Step 6: Optional 10 seconds at 0 A/$cm^2$<br>● Repeat this cycle until reaching 1,000 hrs or the cut-off voltage of 2.2 V/cell.<br>4. At the end of test, measure an I-V curve as detailed in the Measurement of Stack Current-Voltage Curve Procedure (Current Range: 2 mA/$cm^2$ – 1 A/$cm^2$; cut-off 2.2 V). | |
| **Temperature** | Set as required, must be recorded and reported | |
| **Pressure** | Ambient pressure is used in this procedure | |
| | Cut-off voltage in this procedure is set to 2.2 V | |
| **METRIC** | **FREQUENCY** | **TARGET** |
| **Monitor pH and analyse metallic ions release in the recirculating water/solution.** | Continuously or every 100 hrs of steady-state operation from the beginning of the test. | No target for monitoring |
| **Monitor conductivity the recirculating water/solution** | Continuously or every 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 3% $H_2$ in $O_2$ | $H_2$ concentration in the oxygen stream <1 vol% at specific pressure and current |

| | | |
|---|---|---|
| **Voltage Degradation** | 1,000 hrs of operation after first I-V curve. | ≤10 µV/hr degradation in operating voltage using line of best fit and excluding the first 100 hrs of conditioning. |

Performance decay is measured as voltage increase vs. time from BoT and EoT polarisation curves at 1 A $cm^{-2}$

This procedure takes into account the specific targets of the ANIONE project as reported in the DoA i.e. a partial load operation, from 10 % to 100% and a nominal operating current of 1 A $cm^{-2}$ (100% load).

# 4 Efficiency determination:

Overall efficiency is determined from the product of voltage efficiency and faradaic efficiency (under exothermic mode operation). Efficiency is in general determined according to:
G. Tsotridis, A. Pilenga in "EU harmonised terminology for low temperature water electrolysis for energy storage applications", Publications Office of the European Union Publisher, ISBN: 978-92-79-90387-8 (online), 978-92-79-90388-5 (print).

The relevant formulas are reported below:

## Overall efficiency

**Efficiency calculations are based on the High Heating Value and Enthalpy content** $\Delta H^0 = \Delta G^0 + T\Delta S^0$

The total efficiency $\eta_{\omega}$ is defined as the product of energy efficiency and faradaic efficiency values.

$$\eta_{\omega}^{cell} = \varepsilon_{cell} \cdot \eta_I^{cell}$$

(cell overall efficiency)

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

(stack faradaic efficiency)

$$\varepsilon_{cell} = \frac{n \cdot F \cdot U_{tn}}{n \cdot F \cdot U_{cell}} = \frac{U_{tn}}{U_{cell}} < 1$$

Energy (cell efficiency exothermic case )

$$\eta^{HHV} = \frac{HHV}{P_{thermal} + P_{electrical}} \cdot \dot{n}_{H_2}$$

(overall stack efficiency)

# 5 Risk Register

At this stage, no risks linked to D2.1 have been identified.

However, some update of these protocols is envisaged after the first period of experimental activities.

| Risk No. | What is the risk | Probability of risk occurrence[1] | Impact of risk[1] | Solutions to overcome the risk |
|---|---|---|---|---|
| **WP2** | Some protocols may require an updated after the first period of experimental activities | medium | medium | Update specific protocols according to the experimental evidence |

(1) Probability risk will occur and its impact: 1 = high, 2 = medium, 3 = Low

## 6 Conclusions

The protocols and procedures reported in D2.1 have been defined to provide appropriate means of verification for assessing the progress made in the ANIONE project.

The procedures reported here include specific assessment of membranes, catalysts, MEAs and stack.

The aim was to provide a systematic approach to test materials, components, and devices in order to validate them for AEM electrolysis application.

Dynamic tests are also provided to allow for a preliminary evaluation of the capability of an AEM electrolysis system to operate under real life applications.

These protocols are also used to assess the achievements of the project milestones, in particular the targeted performance, efficiency and stability characteristics of AEM electrolysis devices.

Moreover, several procedures have been defined to identify the behaviour of specific components inside devices such as cells and stack. Accordingly, the results from the assessment of cells and stack can provide feed-back and indications on how membrane, electrocatalysts, assembling procedures, housing components can be improved.

The protocols and procedures have been organised also to allow comparing stack and single cell performance and stability at specific current densities. This to get insights into scaling up aspects.

Stack assessment also provide a procedure for determination of the energy consumption or efficiency at the nominal production capacity.

Specific efforts have been addressed to protocols for assessing performance degradation in terms of terminal voltage increase in steady-state and dynamic tests.

The chapter on the “harmonised MEA assessment in single cell” includes several MEA assessment procedures agreed among three H2020 FCH JU projects i.e., ANIONE, CHANNEL AND NEWLY.

These protocols will be updated during the projects life-span as a function of the results achieved for the new developed AEM components and systems.

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