



Improved Durability and Cost-effective Components for New Generation Solid Polymer Electrolyte Direct Methanol Fuel Cells

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DELIVERABLE REPORT

D.2.3 – PROTOCOLS FOR MEA CHARACTERISATION

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PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
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NATURE OF THE DELIVERABLE

R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY	
Keywords	<i>MEAs, Characterisation, Protocols</i>
Abstract	<p>The present deliverable defines characterisation and test protocols for the assessment of performance and durability of MEAs for DMFCs. Steady-state testing conditions and accelerated procedures have been considered to evaluate methanol/catalyst cross-over during normal and prolonged operation, and to assess relevant properties in terms of catalytic activity and durability of the newly developed DMFC electrocatalysts.</p> <p>Specific attention has been devoted to freezing/thawing cycling to assess the achievement of project milestones under specific applications.</p> <p>The procedures used as means of verification to assess the achievement of project milestones are identified.</p>

REVISIONS			
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0.1	26/06/2012	T. Malkow	Improvements
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0.4	13/07/2012	S. Specchia	Figures and parameters

D.2.3 – PROTOCOLS FOR MEAs CHARACTERISATION

I. INTRODUCTION

This deliverable concerns with:

- Individuation of appropriate testing protocols for DMFCs MEAs, to screen the best performing MEAs prepared with different electrocatalysts and methods. The protocols include steady-state, accelerated durability tests and freezing/thawing cycling as well as performance evaluation in relation to the specific applications.
- Establish a benchmark of baseline components against which progress may be assessed in terms of durability, performance and cost.
- Find out correlations between composition, property and performance from ex situ electro-catalysts properties and in situ MEA evaluation data.
- Propose a harmonised protocol testing that can be even agreed, shared and adopted by other labs, not belonging to the DURAMET consortium, for characterizing DMFC's MEAs in the same way, to make easier the benchmarking and comparison of the obtained results by different research groups.

The protocols have been developed following similar criteria already developed for hydrogen-fed PEMFCs under the FCTESQA Project [1]. FCTESQA (Fuel Cell Systems Testing, Safety & Quality Assurance), which is a Specific Targeted Research project (STREP) co-financed by the European Commission within the Sixth Framework Programme, with the main aim of addressing the aspects of pre-normative research, benchmarking, and validation through round robin testing of harmonised, industry-wide test protocols and testing methodologies for fuel cells. The FCTESQA web site, in fact, hosts the internationally agreed harmonised test procedures applicable to fuel cells, stacks, and systems, which were the output of the FCTESQA predecessor project (Fuel Cell Testing and Standardisation Network, FCTESTNET). Moreover, even the DOE protocols [2] and the most relevant [3–25] literature references have been used to set the present protocols.

The DMFC's MEAs testing procedures proposed in the present protocols represent the first attempt of a set of harmonised procedures to be used for benchmarking analysis and comparison of the results among different laboratories and research centres, not strictly belonging to the DURAMET consortium. These protocols are here presented with the aim of proposing harmonized procedures, common for the DMFCs community, to establish agreed and shared “modus operandi” among different Universities and Research Centres working in the same field. Of course, the use of this proposed protocol is not mandatory, and each research entity is absolutely free in partially or fully adopting these rules, by adapting them to the possessed testing facilities.

It will be proposed to insert the present testing protocol within the framework of the FCTSEQA Project, to offer harmonized procedures even for DMFCs, which are missing at the moment, in order to complete the series of harmonized protocols referring to PEFCs, SOFCs, and MCFCs [1].

II. PROTOCOLS

1. MEAs preparation

The following protocol allows the preparation of MEAs according to a standard procedure:

1. Prepare the electrodes: the in-house prepared electrocatalysts can be mixed with 15–33 wt. % Nafion ionomer (suggested baseline ionomer: 5 wt. % solution by Du Pont) and deposited by a doctor blade technique onto a gas diffusion layer (suggested baseline GDL: LT-ELAT by E-TEK even if not anymore commercial, for those labs who still have them available; or standard SGL with microporous layer by The Carbon Group Company). Commercial unsupported electrocatalysts can be used as references (suggested baseline catalysts: Pt-Ru black 1:1 atomic ratio for the anode and Pt black for the cathode by Alfa Aesar); suggested reference catalyst loading: 3 mg cm^{-2} on both anode and cathode, with the aim to reduce the precious metals loads to the levels defined by the project targets. Active area will be 5 or 25 cm^2 for screening of new formulations; from 50 to 180 cm^2 for further validation. Later on the catalyst loading will be reduced up to an acceptable performance level.
2. Prepare the membrane-electrode assemblies: MEAs can be formed by hot-pressing the electrodes on either sides of a pretreated Nafion membrane at $150\text{--}160 \text{ }^\circ\text{C}$ at 25 kg cm^{-2} for 3 min (suggested baseline membrane: Nafion by Du Pont). Alternative membranes can be used to assess alternative materials: temperature, timing and pressure for hot-pressing must be carefully checked to assure a good stability of the MEAs.

2. MEAs characterization, short-term stability tests:

The present protocol allows the testing of fresh MEAs according to a standard procedure in the following test sequence (Figure 1).

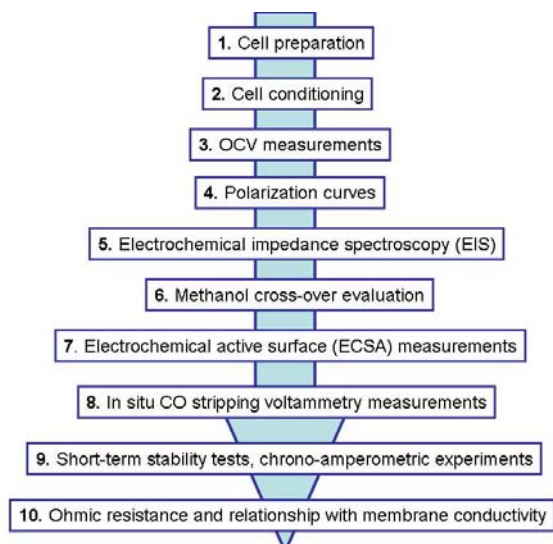


Figure 1. Schematic of test sequences for the MEA characterization in the short term stability tests.

1. Single cell preparation: install the as-prepared MEA in a fuel cell test fixture of 5 or 25 cm² active area (suggested: Fuel Cell Technologies, Inc. single cell hardware)¹ with single serpentine-type flow patterns machined from a high density graphite nuclear grade; close the cell by screwing the retaining bolts with a dynamometric key set at 20-25 kg cm⁻² (for Nafion based MEAs) to guarantee sufficient sealing and good and uniform electrical contact between end plates and the MEA. The 5 cm² cell will serve for materials pre-screening and to provide information relevant for small size DMFC devices operating under passive mode. The 25 cm² cell will be used in conjunction with MEA evaluation for the active mode operation. In the scale-up phase the active area may also vary from 50 to 180 cm² and the reactant flow rates will be adjusted, accordingly.
2. Cell conditioning step: the single cell must be equilibrated at 80 °C with humidified air (100% RH), pre-heated to this same temperature, at the cathode (air flow rate of 350 Nml min⁻¹ for 5 cm² or 1.5 Nl min⁻¹ for 25 cm²; oxygen can be used in alternative by calculating the necessary flow rate) and 1 M of aqueous methanol solution (using deionised / demineralised water) pre-heated to the cell temperature fed to the anode (flow rate of 2 ml min⁻¹ and 350 ml min⁻¹ for 5 cm² cell or 10 ml min⁻¹ and 1.5 l min⁻¹ for 25 cm² cell) at a constant current density of 0.1 A cm⁻² (see for the operating

¹ See, for example, at http://www.fuelcelltechnologies.com/fuelcell/products/single_cell_hardware.asp

conditions Table 1 below). Atmospheric outlet pressure in the anode and cathode compartments is used for all tests concerning with operating temperature below 100 °C. High pressure up to 2 bar,rel can be utilised for high temperature operation depending on the specific membrane characteristics. The conditioning step has to last for 24 hours. Alternatively, the activation can be performed at constant voltage of 0.4 V for 24 hours. — This is only a guideline, and it can be adapted to reach the maximum power performance while keeping good system efficiency.

Table 1. Cell operation conditions during short term stability tests

Quantity (test input)	Symbol	Unit	Value / range
Cell temperature	T_{cell}	°C	80
Oxidant inlet temperature	$T_{\text{ox,inlet}}$	°C	80
Oxidant inlet relative humidity	RH	%	100
Oxidant stoichiometry	λ	-	
Fuel inlet temperature	$T_{\text{fuel,inlet}}$	°C	80
Molar methanol concentration	c_{fuel}	M	1
Methanol flow rate, 5 cm ² cell	Q_{fuel}	ml min ⁻¹	2
Methanol flow rate, 25 cm ² cell	Q_{fuel}	ml min ⁻¹	5
Oxidant flow rate, 5 cm ² cell	Q_{ox}	Nml min ⁻¹	350
Oxidant flow rate, 25 cm ² cell	Q_{ox}	Nml min ⁻¹	1500

- OCV measurement: prior to starting the polarisation curve, the cell voltage is brought to OCV (open circuit voltage). Measure the OCV every second during at least 30 sec but less than one minute (as longer exposure at OCV can irreversibly damage the cell).
- Polarization curves (cell voltage vs. current density or I-V): the main objective of the polarisation curve is to determine the change in the cell voltage (and consequently in the power density) for 1 min generated by variation of the current density (in steps of 2 mA cm⁻² up to 10 mA cm⁻², 10 mA cm⁻² up to 100 mA cm⁻², 50 mA cm⁻² for higher currents). For a cell test at a fixed cell temperature, air inlet temperature can be 5 °C higher to avoid condensation in the case of humid air the current density is preferably increased from 0 (OCV) to the maximum achievable current with a cut-off voltage of 0.2 V (see also Table 2 below). The sampling rate should be 1 Hz in the measurements. The cell voltage (and power density) at a given (averaged) current density is averaged over the last 1 min of the measurements and plotted together with three times its standard deviation (and/or maximum / minimum values as error bars) against the current density. At the end of the I-V curve measurements, the current density will be set to zero (OCV) before stopping all the testing equipments. At all times, the minimum cell voltage should be 200 mV.

Criteria for determining I-V curves:

- Influence of the cell temperature: by maintaining constant feed of the reactants as above, repeat the I-V curve measurements at increasing temperatures from 20 to 90 °C (in steps of 10 °C) for Nafion-based MEAs. Before proceeding with a new temperature step, the cell must be discharged. The cell temperature should be stabilised for minimum 20 minutes before proceeding with the next I-V curve measurement. For MEAs manufactured with membranes different from Nafion (e.g., Phosphonic acid, composite membranes), the maximum temperature could be increased to 150 °C. For APU applications the temperature could be increased up to 160 °C.
- Influence of the methanol concentration (in deionised / demineralised water): by maintaining constant the cell temperature at 60 °C, repeat the I-V curve measurements at increasing methanol concentration of 0.5, 2, 5 and 10 M, respectively. Tests at different molarities can be even performed if of interest.

Table 2. Current density steps in the polarization curve measurements

Current density, mA cm ⁻²	Hold time, min
0 (OCV)	1 min
2 mA cm ⁻²	20 min
4 mA cm ⁻²	20 min
...	
10 mA cm ⁻²	20 min
20 mA cm ⁻²	20 min
....
100 mA cm ⁻²	20 min
150 mA cm ⁻²	20 min
....
200 mA cm ⁻²	20 min
Reverse	
....
0 (OCV)	1 min

5. 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 starting from 0.4 V, or galvanostatic mode starting from 75 mA cm⁻². 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.² In the case of galvanostatic mode, 10% sinusoidal oscillations. The methanol concentration is to varied (0.5, 2, 5 and 10 M) while

² The grid frequency (50 Hz) and its harmonics should be avoided.

maintaining the cell temperature at 60 °C. Additional EIS measurements can be performed with lower and higher air flow rates of e.g., 220 Nml min⁻¹ and 420 Nml min⁻¹ for the 5 cm² cell as well as with oxygen as reactant at the cathode with a flow rate of 81 Nml min⁻¹ (to have the same stoichiometry with respect to 350 Nml min⁻¹ of air flow rate). 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 resistance is determined as per point 10 (below).

6. Methanol cross-over evaluation: methanol cross-over measurements can be carried out electrochemically using respectively 0.5, 2, 5 and 10 M methanol (for 5 cm² cell: 2 ml min⁻¹) at anode side as reference/counter electrode, and He or Ar or N₂ (100 cm³ min⁻¹) at cathode as working electrode. The methanol permeating the MEA would oxidize at the cathode catalyst generating a positive current, which reaches a plateau when the entire methanol is converted into CO₂ (and water) during steady state operation. The cross-over experiments can be carried out by linear sweep voltammetry (LSV) mode with a voltage scan rate of 2 mV s⁻¹ and in the voltage range from 0 to 0.8-V, at a constant cell temperature and inert gas inlet temperature of 60 °C.

An alternative approach is to use the CO₂ sensor method at the cathode to estimate how much methanol crossing the membrane is converted to CO₂. From this value, the methanol cross-over is readily determined. This approach is more accurate with respect to the electro-osmotic drag and will effectively take into account the methanol concentration gradient across the membrane. Both phenomena are related to the operating current density. It will be appropriate to remove water from the cathode outlet stream by using an in-line condenser and a magnesium perchlorate bed to avoid damaging the CO₂ sensor. This method may be affected by CO₂ permeation from the anode through the membrane. For this reason, a comparison of the cross-over values determined by the two methods would be appropriate. The data will be reported both in terms of methanol permeation as mol CH₃OH per min per cm² (milestone MS3) as well as in terms of equivalent cross-over current density.

7. Electrochemical active surface (ECSA) measurements: the main objective of the ECSA curves is to evaluate the microstructural changes (particle agglomeration) and/or chemical degradation of the catalyst during the fuel cell operation. For the anodic ECSA test, the cathode can be used as a dynamic hydrogen electrode when fed with humidified (100 % RH) hydrogen at 100 Nml min⁻¹ (5 cm² cell). The anode will be fed with humidified (100 % RH) nitrogen (or argon) at 300 Nml min⁻¹, then 10 cycles of CV from 0 to 1.1 V at a scan rate of 20 mV s⁻¹ is performed. For PtRu anode catalyst formulations the anodic potential limit will be reduced to 0.5 V to avoid Ru dissolution. The same procedure is reversed and in this case, determination of the cathodic ECSA is performed.

Determination of ECSA is made by integration of the H-adsorption peaks (preferably 0.02–0.4 V DHE, avoiding hydrogen evolution) after subtraction of double layer charging at 0.4 V DHE.

8. In situ CO stripping voltammetry measurements: can be carried out in the single cell DMFC configuration especially for PtRu anode catalysts using hydrogen (1 atm,rel) at the cathode which acts as both counter and reference electrode. For CO stripping, the first, second and third cycles are recorded at 20 mV s^{-1} scan rate after adsorption of CO onto the catalyst using Ar-2 vol-% CO at 0.1 V for 30 min, and subsequent purging in a CO free argon atmosphere for minimum 10-30 min depending on the test bench. Determination of ECSA can be carried out for CO stripping voltammetry (see point 7) and compared with those measurements of point 7.

9. Short-term stability tests, chrono-amperometric experiments: by maintaining the cell voltage at 0.3 V and the cell temperature at $60 \text{ }^\circ\text{C}$, perform test runs with respectively 0.5, 2, 5 and 10 M methanol solutions and air for at least 3 hours. Record the corresponding current density vs. time profiles. Repeat the measurements as per points 4 to 8 (see Figure 1).

10. Ohmic resistance and relationship with membrane conductivity: 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 of the cell. If appropriate a proper equivalent electric circuit model will be applied. This will be subtracted by the resistance contribution of electrodes and hardware measured in a separate test without membrane. The membrane conductivity will be thus determined by normalising the results by the membrane thickness and electrode area. This approach will allow getting information about the conductivity of membrane under the actual operating conditions. It will provide interface resistance assessment by comparing the values determined in situ under OCV with those measured ex-situ in a conventional conductivity set-up defined in WP3 (deliverable D2.2). In situ conductivity will be measured as a function of the operating current density (this influences the electro-osmotic drag) and in the presence of different methanol solutions. For a proper comparison of the in situ data, it will be necessary to report all operating conditions including temperature, reactants, cathode humidification, outlet pressure for both electrode compartments and current density.

11. Both conductivity data and in situ methanol cross-over measurements during MEA characterization will serve to evaluate the membrane selectivity for DMFC applications under practical operating conditions. The selectivity calculated as the ratio between conductivity and methanol cross-over ($\text{mS min cm mol}_{\text{fuel}}^{-1}$) will be used as a relevant parameter for membrane screening.

3. MEAs characterization, long-term stability tests:

The following protocols allow the testing of MEAs subjected to ageing standard procedures.

1. Dynamic load cycling ageing test (Figure 2): this protocol allows testing the voltage and the power as a function of the current density following a dynamic profile versus test duration. The main objective is to determine the evolution of voltage on current load in terms of cell voltage degradation (or cell voltage deviation per operated hour), $\Delta V/\text{hour}$ and power degradation (or power deviation operated hour), $\Delta P/\text{hour}$ when submitting the cell to a specific load profile, including low power and high power settings corresponding respectively to two current densities identified as $i_{\text{load,min}}$ and $i_{\text{load,max}}$ (see Table 3 also below). The test is under galvanostatic control with a load profile at fixed operating temperature and gas conditions. The cell voltage must be stable before starting with the test. less than 5% variation Since polarization curves will be performed at given intervals of time (e.g., every 2 hours), it is possible to determine also the evolution of the OCV.

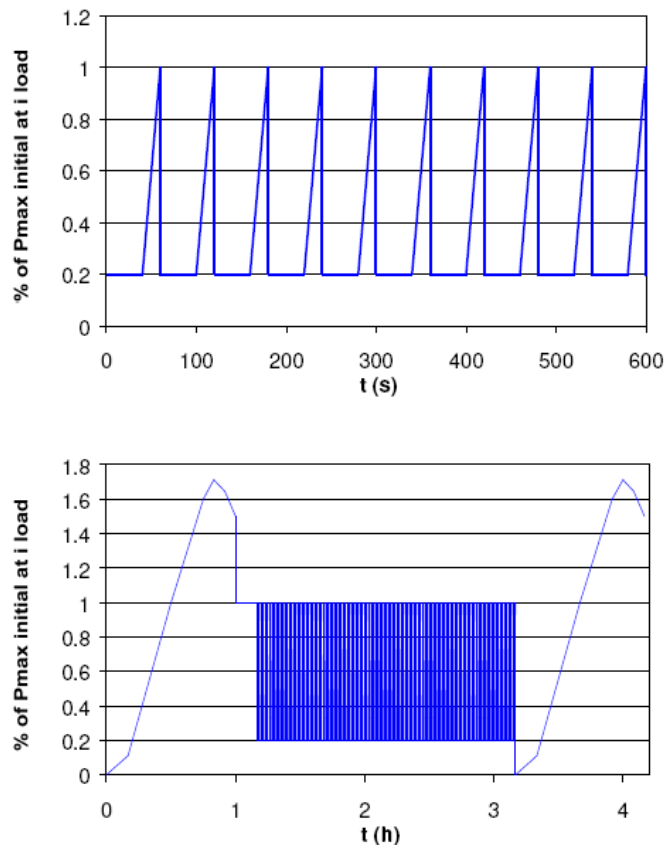


Figure 2. Schematic of the dynamic load cycling ageing test: relative power during dynamic cycling phase over 600 seconds (up) and an initial 1 hour polarization curve followed by a dynamic cycling phase of 2 hours before another 1 hour polarization curve (down).

An initial polarization curve is performed after stabilization at $i_{load,max} = i @ 100\% P_{max}$ ($A\ cm^{-2}$). The minimum current is defined as $i_{load,min} = i @ 20\% P_{max}$ ($A\ cm^{-2}$). After the initial polarization curve, the current density is fixed at $i_{load,max}$ for a first high power setting for 10 min to stabilize the operating conditions before starting the dynamic cycling phase. Then the dynamic cycling phase is performed with the following current profile:

- low power stationary phase = 40 s @ $i_{load,min}$;
- high power dynamic phase = 20 s by increasing i from $i_{load,min}$ to $i_{load,max}$

The current density between $i_{load,min}$ and $i_{load,max}$ is varied in current density steps of $10\ mA\ cm^{-2}$ (the current density is increased step by step, with regular steps with a dwell time of 2 seconds for all steps; increasing prior to the fuel and oxidant flow rates prevents a too steep decline in cell voltage) or with a current density sweep at a fixed rate of $[i_{load,max} - i_{load,min}]/20\ [A\ cm^{-2}\ s^{-1}]$ (with prior increase of the reactant flow rates).

The polarization curves will be performed at fixed intervals corresponding to $t_{max}/10$ where t_{max} is the maximum duration of the test being 500 hours considering the specific DMFC application. The polarization curve measurements are to be conducted at a sampling rate of 1 Hz.

The comparison of the final polarization curve (cell voltage and power density vs. current density) with the initial polarisation is used to qualify the performance loss of the cell on the entire range of current density of the polarisation curve measurements in order to assist in the analysis of any performance degradation if any. In the case of failure, diagnostic tools using electrochemical methods like cyclic voltammetry, EIS, CO stripping, methanol cross-over evaluation, can be applied.

Table 3. Cell operating conditions during long term stability tests.

Quantity (test input)	Symbol	Unit	Value / range
Cell temperature	T_{cell}	$^{\circ}C$	80
Oxidant inlet temperature	$T_{ox,inlet}$	$^{\circ}C$	80
Oxidant inlet relative humidity	RH	%	100
Oxidant stoichiometry	λ	-	
Fuel inlet temperature	$T_{fuel,inlet}$	$^{\circ}C$	80
Molar methanol concentration	C_{fuel}	M	1
Current density at low power setting		$A\ cm^{-2}$	$i_{load,min} = @ 20\% P_{max}$
Low power setting duration		sec	40
Rate of current density change		$A\ cm^{-2}\ per\ sec$	$[i_{load,max} - i_{load,min}]/20$
Current density at high power setting	i	$A\ cm^{-2}$	$i_{load,max} = i @ 100\% P_{max}$
High power setting duration		sec	20

Alternatively, long term stability tests can be carried out under potentiostatic control at potentials useful for portable or APU applications that for DMFCs may be as low as 0.5 or 0.4 V cell voltage. This is to test the device under conditions close to those providing the peak power output. This is relevant to this specific project. To simulate portable operation, start-up/shut-down cycles should be carried out every 6-8 h.

The power density P (W cm^{-2}) = V (V) \times i (A cm^{-2}) should be calculated as a test output, too. The cell voltage deviation per operated hour, $\Delta V/\text{hour}$ (performance loss rate) is calculated at OCV, and on load, i_{load} as follows:

- $[V_{\text{initial @ } i_{\text{load,min}}} - V_{\text{final @ } i_{\text{load,min}}}] / V_{\text{initial @ } i_{\text{load,min}}}$
- $[V_{\text{initial @ } i_{\text{load,max}}} - V_{\text{final @ } i_{\text{load,max}}}] / V_{\text{initial @ } i_{\text{load,max}}}$

Similarly, the power deviation per operated hour, $\Delta P/\text{hour}$ is calculated as follows:

- $[P_{\text{initial @ } i_{\text{load,min}}} - P_{\text{final @ } i_{\text{load,min}}}] / P_{\text{initial @ } i_{\text{load,min}}}$
- $[P_{\text{initial @ } i_{\text{load,max}}} - P_{\text{final @ } i_{\text{load,max}}}] / P_{\text{initial @ } i_{\text{load,max}}}$

Both rates are expressed as percentage.

2. Ageing on/off cycling test (Figure 3): this protocol allows testing the voltage and the power as a function of the current density following an on/off profile versus time. The test is under galvanostatic control with a load profile at fixed operating temperature and gas conditions. The cell voltage must be stable before starting with the test. Since polarization curves will be performed at fixed intervals, it is possible to determine also the evolution of the OCV. An initial polarization curve has to be performed after stabilization at $i_{\text{load}} = i @ P_{\text{max}}$ (A cm^{-2}). The main objective is to determine the evolution of both OCV and voltage on load in terms of V/hours when submitting the single cell to a specific load profile including “on” and “off” phases of 15 minutes each. After the initial polarisation curve, the current density is fixed again at i_{load} for a first “on” phase of 15 minutes. Then the cycling will follow the following profile:
 - “off” phase = 15 minutes at 0 A cm^{-2} ;
 - “on” phase = 15 minutes at $i_{\text{load}} \text{ A cm}^{-2}$.

It is recommended to increase the current density step by step in order to avoid important voltage drop. The current has to be increased from 0 to i_{load} in four steps of 10 s increasing the current of $i_{\text{load}}/4$ at each step as follows:

- $\frac{1}{4} i_{\text{load}} \text{ A cm}^{-2}$ during 10 s
- $\frac{1}{2} i_{\text{load}} \text{ A cm}^{-2}$ during 10 s
- $\frac{3}{4} i_{\text{load}} \text{ A cm}^{-2}$ during 10 s
- $i_{\text{load}} \text{ A cm}^{-2}$ during 14 min 30 s

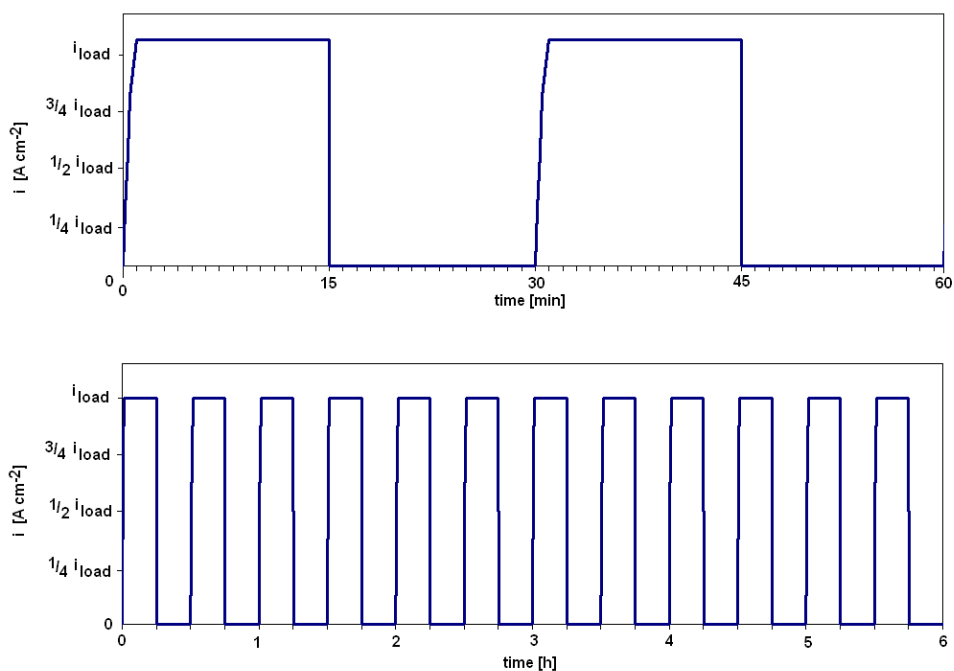


Figure 3. Schematic of the ageing on/off cycling test: relative current density cycling phase over 1 hour (up) and over 6 hours (down).

During the two phases, the flow rates have to be controlled as follow:

- “on” phase: $Q_{\text{fuel}} = Q\lambda_{\text{fuel}}$ and $Q_{\text{ox}} = Q\lambda_{\text{ox}}$
- “off” phase: $Q_{\text{fuel}} = Q_{\text{fuel,min,OCV}}$ and $Q_{\text{ox}} = Q_{\text{ox,min,OCV}}$

Where: $Q_{\text{fuel,min,OCV}}$ and $Q_{\text{ox,min,OCV}}$ correspond to the smallest amounts of reactants necessary to maintain the pressures p_{fuel} and p_{ox} during the “off” phases.

The duration of this test depends on the specific objective of the test and on the related specific “ending” criterion: fixed life time test or fixed performance losses (considering the power, the voltage on load or the OCV). A final polarisation curve has to be performed after the end of the on/off cycling measurement step, unless the performance loss or the components degradation (like membrane failure) does not allow it. As for the initial polarisation curve, the final curve has to be started after an “on” phase at $i_{\text{load}} = i @ P_{\text{max}}$ (A cm^{-2}). The comparison of the final polarisation curve with the initial one will be used to qualify the performance loss of the cell on the entire range of current density in order to analyse the causes of degradation. During the polarisation curve the sampling rate of 1 Hz should be respected (of course, other characterizations using electrochemical methods like cyclic voltammetry, EIS, CO stripping, methanol cross-over and ECSA evaluation, can be applied, following the test sequence reported in Figure 1, points 3 to 9, in order to help understanding the performance evolution).

The power density P (W cm^{-2}) = V (V) x i (A cm^{-2}) should be calculated as a further output for this test and can be calculated for all the measurement steps (polarisation curves and “on” phases).

The voltage deviations ΔV will have to be calculated at OCV and on load over the complete duration of the cycling measurement step in order to evaluate a “performance progression rate” (normally a performance “degradation rate”) $\Delta V_{OCV}/dt$ and $\Delta V_{i_{load}}/dt$:

- $\Delta V_{OCV} = \text{OCV of the first “off” phase} - \text{OCV of the last “off” phase}$
- $\Delta V_{i_{load}} = V @ i_{load} \text{ of the first “on” phase} - V @ i_{load} \text{ of the last “on” phase}$

The performance loss will be calculated in % @ i_{load} as follow:

- $[\text{V @ } i_{load} \text{ of the first “on” phase} - \text{V @ } i_{load} \text{ of the last “on” phase}] / \text{V @ } i_{load} \text{ of the first “on” phase}$
- $[\text{P @ } i_{load} \text{ of the first “on” phase} - \text{P @ } i_{load} \text{ of the last “on” phase}] / \text{P @ } i_{load} \text{ of the first “on” phase}$

4. MEAs characterization, freezing/thawing tests:

The following protocol allows the testing of MEAs subjected to ageing standard procedures according to repetitive freezing/thawing cycles.

1. Freezing/thawing tests: this protocol allows testing the voltage and the power as a function of the current density following a series of consecutive freezing/thawing (F/T) cycles from $-20\text{ }^{\circ}\text{C}$ to $+60\text{ }^{\circ}\text{C}$ versus time. To avoid freezing of the supplied methanol to the cell/stack when the temperature goes below $0\text{ }^{\circ}\text{C}$, it is recommended to work with a methanol solution of at least 8 M at anode side, which avoid freezing up to $-23\text{ }^{\circ}\text{C}$, as shown in Figure 4.

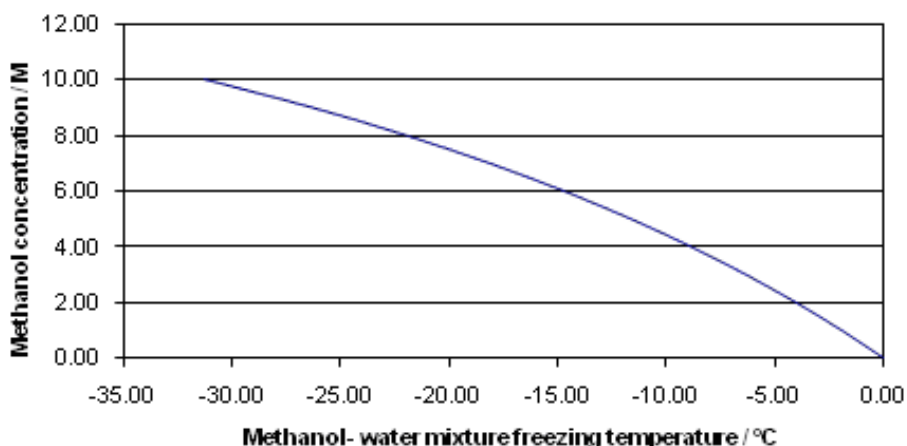


Figure 4. Methanol – water mixture ideal freezing temperature as a function of methanol concentration [26]

The test is under galvanostatic control with a load profile at fixed operating temperature and gas conditions. The cell voltage must be stable before starting with the test. Since polarization curves will be performed at fixed intervals, it is possible to determine also the evolution of the OCV. An initial polarization curve has to be performed after stabilization at $i_{load} = i @ P_{max}$ ($A\ cm^{-2}$). The main objective is to determine the evolution of both OCV and voltage on load in terms of $V\ h^{-1}$ when submitting the single cell to a series of F/T cycles. After the initial polarization curve, the current density is fixed at $i_{load,max}$ for a first high power phase of 10 min to stabilize the cell. Then the cell must be stopped. By maintaining the anode flooded with the methanol solution at high concentration, the stack must be placed in the thermostatic chamber and frozen up to $-20\ ^\circ C$ for 3 h. Then the stack must be heated up to $+60\ ^\circ C$ and a new cycle can start again.

The F/T cycling sequence has to be performed with the following current profile, and repeated cyclically (at least 50 times):

- Polarization curve in galvanostatic way
- Stabilization of the cell/stack at $i_{load} = i @ P_{max}$ ($A\ cm^{-2}$) for 10 min
- Freezing of the cell/stack @ $-20\ ^\circ C$ for 3 h
- Thawing of the cell/stack @ $+60\ ^\circ C$

Just in case, the cathode side of the stack can be purged with an increased air flow rate to remove the water formed during the operating time. The amount of air flow rate to be used and the timing of the purging procedures must be settled on purpose.

The duration of this test depends on the specific objective of the test and on the related specific “ending” criterion: fixed life time test or fixed performance losses (considering the power, the voltage on load or the OCV). A final polarisation curve has to be performed after the end of the last F/T cycle step, unless the performance loss or the components degradation (like membrane failure) does not allow it. As for the initial polarisation curve, the final curve has to be started after an “on” phase at $i_{load} = i @ P_{max}$ ($A\ cm^{-2}$). The comparison of the final polarisation curve with the initial one will be used to qualify the performance loss of the cell on the entire range of current density in order to analyse the causes of degradation. During the polarisation curve the sampling rate of 1 Hz should be respected (of course, other characterizations using electrochemical methods like cyclic voltammetry, EIS, CO stripping, methanol cross-over and ECSA evaluation, can be applied after the end of each F/T cycling step, or at least after the end of every 10 F/T cycles, in order to help understanding the performance evolution).

The power density P ($W\ cm^{-2}$) = V (V) x i ($A\ cm^{-2}$) should be calculated as a further output for this test and can be calculated for all the measurement steps (polarisation curves).

The voltage deviations ΔV will have to be calculated at OCV and on load over the complete duration of the cycling measurement step in order to evaluate a “performance progression rate” (normally a performance “degradation rate”) $\Delta V_{OCV}/dt$ and $\Delta V_{i_{load}}/dt$:

- $\Delta V_{OCV} = OCV \text{ before the first F/T cycle} - OCV \text{ after the last F/T cycle}$
- $\Delta V_{i_{load}} = V @ i_{load} \text{ before the first F/T cycle} - V @ i_{load} \text{ after the last F/T cycle}$

The performance loss will be calculated in % @ i_{load} as follow:

- $[V @ i_{load} \text{ before the first F/T cycle} - V @ i_{load} \text{ after the last F/T cycle}] / V @ i_{load} \text{ before the first F/T cycle}$
- $[P @ i_{load} \text{ before the first F/T cycle} - P @ i_{load} \text{ after the last F/T cycle}] / P @ i_{load} \text{ before the first F/T cycle}$

5. Post-mortem ex-situ MEAs characterization tests:

The following protocol allows the characterization of the MEAs in terms of GDL, catalyst, membrane and backing layer after long-term stability tests and freezing/thawing tests according to a standard procedure. Cross sections of the MEAs can be prepared by freeze-fracturing the entire assembly, previously pre-cut with scissors, after immersion for 10 min in liquid nitrogen.

1. Ex-situ physico-chemical analysis post operation by:
 - SEM-EDX or FESEM/EDX (dissolution into the membrane)
 - TEM (particle size sintering)
 - XPS (surface analysis)
 - XRF (elemental analysis)

6. References:

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