

## CATAPULT

### NOVEL CATALYST STRUCTURES EMPLOYING Pt AT ULTRA LOW AND ZERO LOADINGS FOR AUTOMOTIVE MEAS

Grant agreement no.: 325268

Start date: 01.06.2013 – Duration: 36 months

Project Coordinator: Deborah Jones – CNRS

## DELIVERABLE REPORT

### DELIVERABLE NUMBER 2.1 – OPERATING PROPERTY TABLE FOR MEA AND TEST PROTOCOLS

|                              |  |
|------------------------------|--|
| Due Date                     | 31st August 2013   |
| Author (s)                   | Dr. Hübner, Volkswagen AG, I. Harkness, S. Buche (JMFC), D. J. Jones, J. Rozière, F. Jaouen, S. Cavaliere (UM2-CNRS), H. Gasteiger (TUM) P. Heikkila (VTT) |
| Workpackage                  | WP 2   |
| Workpackage leader           | Dr. Hübner, Volkswagen AG  |
| Lead Beneficiary             | Volkswagen AG  |
| Date released by WP leader   | 12th December 2013   |
| Date released by Coordinator | 16th December 2013   |

### DISSEMINATION LEVEL

|           |   |          |
|-----------|---|----------|
| <b>PU</b> | Public  | <b>X</b> |
| <b>PP</b> | Restricted to other programme participants (including the Commission Services)        |          |
| <b>RE</b> | Restricted to a group specified by the consortium (including the Commission Services) |          |
| <b>CO</b> | Confidential, only for members of the consortium (including the Commission Services)  |          |

### NATURE OF THE DELIVERABLE

|          |              |          |
|----------|--------------|----------|
| <b>R</b> | Report       | <b>X</b> |
| <b>P</b> | Prototype    |          |
| <b>D</b> | Demonstrator |          |
| <b>O</b> | Other        |          |

## SUMMARY

|                 |  |
|-----------------|--|
| <b>Keywords</b> | <i>Specifications, test parameters, test protocols, MEA, MEA components</i>  |
| <b>Abstract</b> | <p><i>The following document is summarizing specifications for MEA development within the CATAPULT project and providing test parameters for the basic components as basis for the material evaluation within the project. Besides input of internal test protocols provided by the WP partners, harmonization efforts presently on the way by the DOE and the EU (JRC) are also considered.</i></p> <p><i>Definition of fuel cell specifications and test protocols is an on-going continuous process; therefore regular updates to this document will be given during the project, if necessary.</i></p> |

## REVISIONS

| <b>Version</b> | <b>Date</b>                   | <b>Changed by</b>      | <b>Comments</b>                                  |
|----------------|-------------------------------|------------------------|--|
| <b>0.1</b>     | 18th July 2013                | Dr. Hübner, Volkswagen | Initiated and draft                              |
| <b>0.2</b>     | 25th July 2013                | Drs Buche and Harkness | JMFC input                                       |
| <b>0.3</b>     | 15th September 2013           | D. Jones               | UM2 CNRS input                                   |
| <b>0.4</b>     | 30th September 2013           | H. Gasteiger           | TUM Input  |
| <b>0.5</b>     | 1st October 2013              | G. Hübner              | Input from telecon                               |
| <b>0.6</b>     | 7th October 2013              | F. Jaouen              | Input for non-PGM catalysts, tables update, edit |
| <b>0.7</b>     | 28th October 2013             | D. Jones               | Edit   |
| <b>0.8</b>     | 4th December 2013             | I. Harkness            | Standard materials defined                       |
| <b>0.9</b>     | 12th December 2013            | P. Heikkila            | VTT input  |
| <b>0.10</b>    | 12th December 2013            | G. Hübner              | Finalised  |
| <b>0.11</b>    | 28 <sup>th</sup> January 2014 | G. Hübner              | Input M6 project mt                              |
| <b>0.12</b>    | 23 <sup>rd</sup> June 2014    | G. Hübner              | Update test protocol and downselection criteria  |

---

# OPERATING PROPERTY TABLE FOR MEA AND TEST PROTOCOLS

---

The first objectives of WP2 are to capture the current application specifications for materials and MEAs, integrating Auto-Stack recommendations, agree protocols for MEA characterisation in automotive drive cycles. In later stages of the project, a stack integrating MEAs comprising CATAPULT catalyst components will be assembled and tested with simulated power profiles. WP2 will also develop a plan for use of results using the output from its techno-economic assessment.

This deliverable report provides a summary of the DoE and AutoStack specifications for automotive MEAs. It describes the test conditions that will be used to screen MEAs comprising CATAPULT materials, as well as accelerated stress tests for use on down-selected samples. The report also outlines the testing methods for MEA components available for use within the CATAPULT partnership, and provides protocols for electrochemical characterisation of catalysts and catalyst supports.

## Content

- 1 Principal Specifications for MEAs
  - 1.1 MEA test protocols
  - 1.2 MEA test protocols for use in CATAPULT
- 2 *In situ* analytical methods and test methods available in CATAPULT
- 3 Component testing

## 1. Principal Specifications for MEAs

Besides achieving performance targets at pre-specified operating conditions for an automotive MEA there are two further key properties, which need being considered in the very early concept phase of a new MEA design: robustness and durability.

Robustness means stability in operating performance over a wide range of operating conditions and level of performance loss in, in case of deviation from ideal operating conditions. Although performance break in does not mean irreversible damage of the MEA, it can be critical for a fuel cell system in a vehicle. If for example a MEA design has the tendency to condense water internally, this may lead to considerable performance loss at lower temperature and at certain operating conditions. Water condensation or retention in a MEA on the other hand may enable a system simplification due to removal of the requirement for an external humidifier. It may also be advantageous at elevated operating temperature in order to enable operation close to (or above) the water evaporation temperature. An ideal MEA enables stable operating performance at a wide range of operating conditions.

Durability of a MEA means low irreversible performance loss. Irreversible performance loss is generally traceable back to catalyst and catalyst support degradation as well as thinning of the membrane material in the process of operation. It therefore basically is a material issue. Irreversible performance

loss can also be a result of frequent or severe occurrences of cell reversal, e.g. water condensation in the anode can lead to fuel starvation and result in fatal catalyst corrosion. Of course, many degradation modes like the start stop degradation can be coped with partially through selection of an operating strategy, however in order to drive down vehicle costs, a simplification of the vehicle architecture is necessary, requiring more stable materials in the MEA.

Precious metals have a very strong contribution to the present fuel cell vehicle costs. In fact a state of the art 100 kW fuel stack of the present technology generation contains roughly 70 g Pt worth 2.000 €. This is 10 times higher loading than the one required for fulfilling the outstanding EURO 6 exhaust legislation for Diesel vehicles. Therefore the combination of the low precious metal loading goals of this project with the necessary performance, robustness and durability demands seems to be the critical target of this project.

In the US, the DOE has been working on a harmonisation of the MEA specification for quite some time, in the EU similar harmonisation attempts have just been started. MEA specifications for automotive MEAs have recently been concluded in the AUTOSTACK project. This project however has been focused on the next stack generation with a prognosis for development readiness in the time frame 2015 – 2020. Therefore the MEA technology considered was rather conservative with a recommended Pt loading in the range 0,3 – 0,6 mg/cm<sup>2</sup> (1 W/cm<sup>2</sup> at 0,675 V and 0,2 A/cm<sup>2</sup> at 0,8 V). As a result a lower precious metal loading was seen as being critical, to drive down the overall stack and system costs. Table 1 summarises the DoE and Autostack targets and gives some outlook on the long term automotive targets:

Table 1.

|   | DOE 2017 target                 | DOE 2020 target                 | Draft Autostack II target (2013)   | Automotive long term targets  |
|---|---------------------------------|---------------------------------|--|---|
| Performance at peak power                                 |                                 |                                 | 1.2 W/cm <sup>2</sup> at 0.6 V   |   |
| Performance at rated power                                | 1 W/cm <sup>2</sup>             | 1 W/cm <sup>2</sup>             | 1 W/cm <sup>2</sup> at 0.675 V   |   |
| Performance at 0,8 V                                      | 0.3 A/cm <sup>2</sup>           | 0.3 A/cm <sup>2</sup>           | 0.2 A/cm <sup>2</sup>  |   |
| Max. operation temperature                                | 120 ≥ 95°C                      | 120 ≥ 95°C                      | 95°C (coolant outlet)  | 110°C (duration certain percentage of lifetime, cumulative)   |
| Max. Operating pressure                                   |                                 |                                 | 2 bar(abs)   | 1.5 bar(abs)  |
| Humidification  |                                 |                                 | Anode:<br>30 - 60 %<br>Cathode:<br>30 - 50 %                               | No external humidification (MEA internal water retention?);<br>Tolerance to humidity/<br>water condensation |
| Stoichiometry   |                                 |                                 | H2: 1.3 – 1.5<br>Air: 1.6 – 1.8  | H2: 1.3<br>Air: 1.5   |
| Maximum permitted pressure difference (anode and cathode) |                                 |                                 | 170 mbar   |   |
| Pt group total loading                                    | 0,125 mg/cm <sup>2</sup> (g/kW) | 0,125 mg/cm <sup>2</sup> (g/kW) | Phase I: 0.53-0.63 mg/cm <sup>2</sup><br>Phase II: 0,32 mg/cm <sup>2</sup> | ≤ 0.125 mg/cm <sup>2</sup>  |

|  |                                 |                                 |   |  |
|--|---------------------------------|---------------------------------|---|--|
| <b>Stack Unassisted start from</b> (minimum operating temperature MEA) | -30°C                           | -30°C                           | -25°C   | - 30°C   |
| <b>Freeze temperature performance availability of MEA</b>              |                                 |                                 | Cold start up time to rated power: 30 sec.                      | -28°C: ≥ 20 % Pmax<br>-15°C: ≥ 40 % Pmax<br>- 5°C: ≥ 60 % Pmax |
| <b>Durability with voltage cycling</b>                                 | 5000 hrs                        | 5000 hrs                        | 5000 hrs  | ≥ 5000 hrs   |
| <b>Cell reversal allowed</b>   |                                 |                                 | no  | Yes, tbd.  |
| <b>Start Stop tolerance</b>  |                                 |                                 |   | Yes, tbd.  |
| <b>Minimum allowed cell voltage</b>                                    |                                 |                                 | 0,2 V   |  |
| <b>Max. allowable voltage (idle/stand by)</b>                          |                                 |                                 |   | 0.95V/0.9V, time tbd.  |
| <b>Loss in initial catalytic activity</b>                              | < 40 % mass activity loss       | < 40 % mass activity loss       | < 10 % power loss at nominal (0.635 V/1.415 A/cm <sup>2</sup> ) |  |
| <b>Electro catalyst support stability</b>                              | < 10 % mass activity loss       | < 10 % mass activity loss       |   |  |
| <b>ORR Mass activity</b>   | 0.44 A/mg Pt at 900 mV          | 0.44 A/mg Pt at 900 mV          |   | 1.1 A/mg Pt at 900 mV ("10x ORR catalyst")                     |
| <b>Non Pt catalyst ORR activity per volume of electrode</b>            | 300 A/cm <sup>3</sup> at 800 mV | 300 A/cm <sup>3</sup> at 800 mV |   |  |

The following project targets are seen as relevant for the down selection of the MEAs developed in the project:

Project Performance targets:  
0,65 V: ≥ 1,2 A/cm<sup>2</sup> (H2/air)

Fullfilling > 80 % of the Poject Performance targets is seen as selection criteria for further analysis of the MEAs and consideration as candidates for the later automotive single cell and short stack integration.

These candidates will undergo the following tests:

- evaluation of freeze damage + <0°C performance availability
- application of durability test protocolls (see section.....)

## 1.1 MEA test protocols

Harmonising test protocols and establishing some early round-robin sample evaluation must clearly be seen as one of the prerequisites for the evaluation of the materials developed within CATAPULT. At the moment several efforts are made by the Fuel Cells and Hydrogen Joint Undertaking to come to a common understanding of the MEA and MEA component evaluation processes in European funded projects. Recently Georgios Tsoitridis of JRC has started an initiative to collect OEM internal test protocols and try to agree some harmonisation of the protocols. This approach is a step in the direction of standardising the evaluation process of PEM fuel cell technology and is very important for a subsequent market introduction of the fuel cell technology. Similar attempts have been undertaken in the past for batteries and battery materials and in fact the tests developed there are now used by most end users and battery developers. For fuel cells the DOE started this process. Therefore in the following paragraph we will give an overview on the test protocols recommended by the DOE and the status of

the JRC attempt. Because the JRC initiative is still in the process of setting up, we will give an update on their test protocols from time to time.

As mentioned in 2.1.1, three different MEA properties need to be addressed: performance, robustness and durability. Performance evaluation is usually determined using some standard reference operating conditions. Regarding robustness, ideally a broad operating parameter window, including separately regulated anode and cathode humidity, operating pressure, stoichiometry and voltage/current would be ideal. Thus the best point of operation for each MEA and the operating robustness at each parameter set could be identified. This would of course lead to an enormous amount of data and a very long resulting measuring time. Therefore for this project we, besides a reference performance curve, will use two additional polarisation curves, one at dry, the other at wet operating conditions. This will enable to evaluate the MEA performance in critical operating parameters.

For the evaluation of MEA durability, there is a very promising set of accelerated ageing tests developed by DoE. These tests are very specific for the particular MEA components and therefore enable the evaluation of the individual electrode catalyst, catalyst carrier or membrane. VW recommends using these tests for the durability evaluation of the materials developed within CATAPULT.

In the last JRC meeting it was seen as critical to directly apply a drive cycle to a MEA test cell. These drive cycles usually are applied for determination of a balanced fuel consumption (average of town, motor way, country road). For a fuel cell test they are critical and not relevant as long as tests are made in small single cells and short stacks, only; on the one hand only a few test stands are really dynamic enough to follow a fast automotive load cycle, regarding voltage changes and gas humidity supply, on the other hand the effecting degradation event would be a mixture of several degradation events (start/stop, fuel starvation, high potential, voltage cycling) and therefore are not so easy to interpret as the specific DoE accelerated ageing cycles. Therefore it was decided, to come up with a simplified dynamic load cycle based on the NEDC (New European Driving Cycle). The parameters for this cycle can be found in Figure 1, it needs to be further discussed in how far they will be used for CATAPULT. However, at the moment, these protocols are not fully finalized by JRC, yet.



PEMFC single cells for FCH-JU supported projects for automotive applications



## Durability test protocols

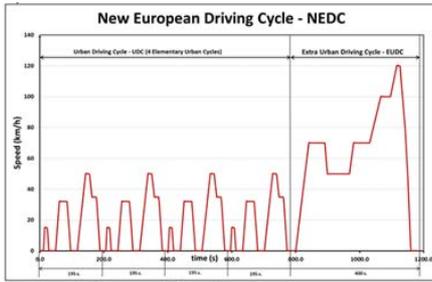


Figure 4:  
NEDC profile according to EU Directive 98/69/CE

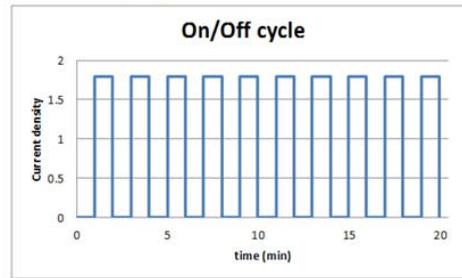


Figure 6:  
On/off load cycle

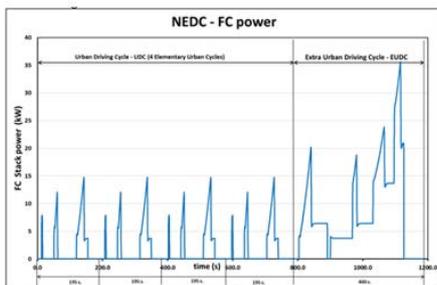


Figure 5:

## Dynamic cycle testing

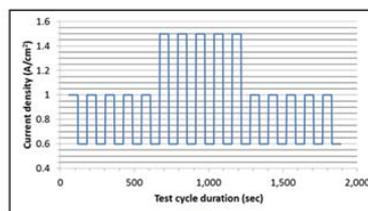


Fig. 7  
Dynamic Testing - Test 1

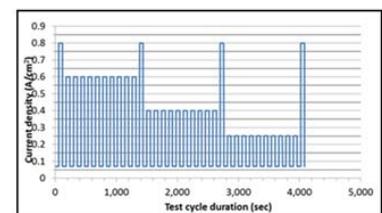
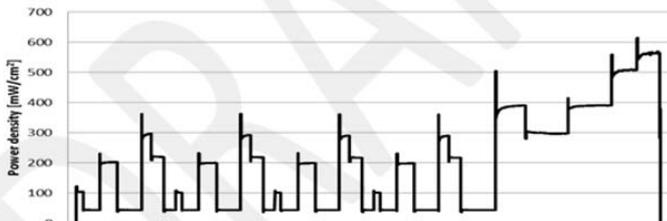


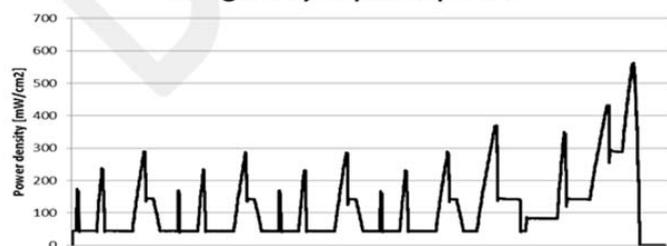
Fig. 8  
Dynamic Testing - Test 2

### Rectangular cycle power profile



Rectangular profile easier to be translated, but not so realistic.

### Triangular cycle power profile



Triangular profile more realistic, but danger of drying out the MEA at long idle times.

Regarding the EU operating parameter harmonization there is a suggestion for future operating parameter harmonization. The following tabel is giving an overview on the MEA operating parameters as a summary of the input from the EU automotive OEMs (Input from JRC meeting, Tuesday 1st April 2014)

The Load Cycle is still in the process of harmonization among the FCH JU OEMs.

|       | Test input                            | Symbol          | Unit | Values  |
|-------|---------------------------------------|-----------------|------|---|
|       |                                       |                 |      | Low Temp. PEM   |
| ANODE | Nominal cell operating temperature    | $T_{cell}$      | °C   | 80  |
|       | Fuel gas inlet temperature            | $T_{fuel,in}$   | °C   | 85  |
|       | Fuel gas inlet humidity               | $RH_{fuel,in}$  | % RH | 50  |
|       | Fuel gas inlet pressure (absolute)    | $P_{fuel,in}$   | kPa  | 250   |
|       | Fuel gas composition                  | $X_{H_2, fuel}$ |      | H <sub>2</sub> 5.0 quality (<0.5 ppm CO, <0.5 % N <sub>2</sub> , <0.5 ppm CO <sub>2</sub> ) |
|       | Fuel stoichiometry                    | $\lambda_{H_2}$ | -    | 1.3   |
| CATH  | Oxidant gas inlet temperature         | $T_{air,in}$    | °C   | 85  |
|       | Oxidant gas inlet humidity            | $RH_{ox,in}$    | % RH | 30  |
|       | Oxidant gas inlet pressure (absolute) | $P_{ox,in}$     | kPa  | 230   |

|  | Test input  | Symbol         | Unit              | Values   |
|--|---|----------------|-------------------|--|
|  |   |                |                   | Low Temp. PEM  |
|  | Oxidant   | $X_{Air, Ox}$  | -                 | <500ppm CO <sub>2</sub> , ≤10ppm CO, ≤2.5 ppm NO <sub>x</sub> , ≤5ppm SO <sub>2</sub> , ≤0.01 mg/m <sup>3</sup> Oil) |
|  | Air stoichiometry                                   | $\lambda_{Ox}$ | -                 | 1.5  |
|  | Minimum current density for stoichiometry operation | $J_{min}$      | A/cm <sup>2</sup> | 0.2  |

|         | Test input (stressor)                |                     | Operating conditions |  |              |     |
|---------|--------------------------------------|---------------------|----------------------|--|--------------|-----|
|         | Symbol                               | Unit                | Low setting          | Reference setting  | High setting |     |
|         | Nominal cell operating temperature   | $T_{cell}$          | °C                   | 45   | 80           | 95  |
| ANODE   | Fuel gas inlet temperature           | $T_{fuel,in}$       | °C                   | 50   | 85           | 100 |
|         | Fuel gas inlet humidity RH           | $RH_{fuel,in}$      | %                    | 25   | 50           | 85  |
|         | Fuel gas inlet pressure (absolute)   | $P_{fuel,in}$       | kPa                  | 160  | 250          | 300 |
|         | Fuel gas composition                 | $X_{H_2, fuel}$     | -                    | H <sub>2</sub> 5.0 quality (<0.5 ppm CO, <0.5 % N <sub>2</sub> , <0.5 ppm CO <sub>2</sub> )                                  |              |     |
|         | Fuel inlet stoichiometry             | $\lambda_{H_2}$     | -                    | 1.1  | 1.3          | 1.5 |
| CATHODE | Oxidant gas inlet temperature        | $T_{air,in}$        | °C                   | 50   | 85           | 100 |
|         | Oxidant gas inlet humidity           | $RH_{Ox,in}$        | %                    | 20   | 30           | 85  |
|         | Oxidant inlet pressure (absolute)    | $P_{Ox,in}$         | kPa                  | 140  | 230          | 280 |
|         | Oxidant                              | $X_{Air, Ox}$       | -                    | Air (<500ppm CO <sub>2</sub> , ≤10ppm CO, ≤2.5 ppm NO+NO <sub>2</sub> , ≤5ppm SO <sub>2</sub> , ≤0.01 mg/m <sup>3</sup> Oil) |              |     |
|         | Oxidant inlet stoichiometry          | $\lambda_{Ox}$      | -                    | 1.3  | 1.5          | 2.0 |
|         | Oxidant-to-fuel pressure difference* | $P_{fuel, Ox,diff}$ | kPa                  | -20  | -20          | -20 |

Additional analytical methods: Besides the recording of polarisation curves, impedance spectroscopy and cyclic voltammetry are recommended as further analytical tools in order to gain further insight into the cell limitations and degradation effects of both electrodes and MEA.

Table 2 summarises the reference polarisation curve/performance determination (1 and 3) and a temperature variation test (2) protocols available by DOE and JRC-ET. The JRC-ET protocols are currently undergoing a process of harmonisation, so further updates are expected in the near future.

| ID  | Scan range         | Scan rate   | number | anode                    | cathode                  | values                                      | temperature                              | pressure | humidity                          | source              |
|---|--------------------|---|--------|--------------------------|--------------------------|---|--|----------|-----------------------------------|---------------------|
| Performance Control (humidity, temperature) | polarisation curve | 0.02 A/cm <sup>2</sup> /min up to 100 mA/cm <sup>2</sup> to 0.04 A/cm <sup>2</sup> /min bis 1.5 A/cm <sup>2</sup> oder >0.4 V | 1      | H <sub>2</sub> (s = 1.2) | Air (s = 2)              | VIR curve, ECSA, H <sub>2</sub> -cross, HFR | 60°C, 80°, 90°C                          | 150 kPa  | Dew point 80°C/80°C and 64°C/64°C | JRC-ET <sup>°</sup> |
| Performance Control (temperature)           | fixed voltage      | U: bei 0.6 und 0.12 A/cm <sup>2</sup> wenn >0.35 V  | 1      | H <sub>2</sub> (s = 1.2) | Air (s = 2)              | U, HFR                                      | 64, 75, 80, 85, 90, 95, 100, 105, 110 °C | 150 kPa  |                                   | JRC-ET <sup>°</sup> |
| Performance Control (humidity)              | polarisation curve |   | 1      | H <sub>2</sub> (s = 1.5) | O <sub>2</sub> (s = 1.8) |   | 80°C                                     | 150 kPa  | 40 % / Dew Point 59°C             | DOE*                |

Table 2. Reference polarisation curve/performance determination (1 and 3) and a temperature variation test (2) protocols (DOE and JRC-ET)

\*U.S. DRIVE Partnership, Cell Component Accelerated Stress Test and Polarization Curve Protocols for Polymer Electrolyte Membrane Fuel Cells, Revised December 16, 2010, ([http://www.uscar.org/commands/files\\_download.php?files\\_id=267](http://www.uscar.org/commands/files_download.php?files_id=267))

<sup>°</sup>European Commission, Joint Research Centre

In order to evaluate MEA robustness, ideally a wide parameter field is preferred covering a variety of different operating parameters. Fig. 2 gives data of a humidity variation, covering humidities from 20 – 100 % on anode and cathode side, respectively. This gives a very characteristic plot for every particular CCM GDL combination. It enables to determine the best point of performance as well as operating robustness of the particular MEAs:

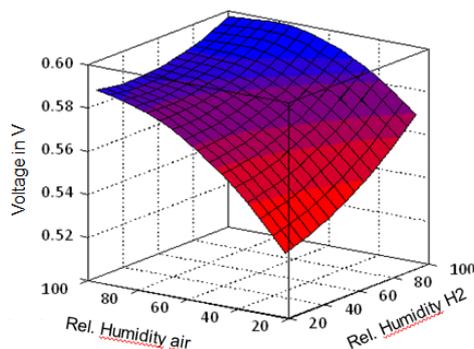


Fig. 2: Voltage at 1,0 A/cm<sup>2</sup> at various humidification values

However in order really to get representative picture of the MEA qualification, it would be necessary to add further current and also pressure and stoichiometry values. This would end up in a very large parameter field consuming lots of measurement time.

## 1.2 MEA test protocols for use in CATAPULT

### Standard MEA components for use in CATAPULT:

**Membrane:** The standard membrane for this programme is a proprietary JM membrane of 17-20  $\mu\text{m}$  thickness which consists of a low equivalent weight PFSA and a reinforcement web. A large quantity has been reserved so that most of the requirements for the complete programme can be met from a single batch. The optimum conditions for decal transfer or bonding of electrodes will be material and equipment dependent and thus should be determined by each partner. Based on JM's experience it would be expected that the conditions will fall within the range of 150-190  $^{\circ}\text{C}$  and 400-800 psi applied load. Generally the lamination should be for 1-3 minutes and cooling with the load still applied is recommended.

**Anode:** JM have agreed to supply a standard anode print on PTFE for decal transferring. This will be a low loaded part (nominal loading 0.1  $\text{mg}/\text{cm}^2$ ) with a platinum loading of 60 wt% on carbon. The layer design has been optimised for anode performance so these layers should not be used as cathodes as the performance will be very poor.

**GDL:** It has been decided that testing will not be limited to a single GDL, but JM have agreed to supply a JM proprietary GDL based on Toray TGP-H-060, if required. This GDL is usually used as an internal reference material at JMFC, but is not a current standard product. It was thought best if partners initially test with a GDL they are comfortable with in their hardware and then possibly investigate alternatives to optimise performance at a later stage. TUM currently test with SGL 25 BC. JM can test with a range of GDLs. The Toray-based material is usually used as a baseline, but other GDLs are used depending on the apparent water management of the catalyst coated membrane design.

### 1.2.1 Pt-based catalysts

#### Break in procedure

Consistent conditioning of MEAs is critical for obtaining comparable MEA performance data across all CATAPULT research groups. For new and untested materials, this MEA conditioning (ramp-in) will be done under voltage-control in single cells (4-50 cm<sup>2</sup>) which is the most robust ramp-in procedure (avoiding unintentional cell reversal). For further developed materials which will be tested in short stacks, a current-controlled ramp-in procedure will be used, which however is designed to mimic the voltage-control mode used for single cell materials screening. The operating conditions for both ramp-in procedures are 60 °C, 100%RH, 150 kPa<sub>abs</sub> gas inlet pressure and constant hydrogen/air (oxygen for mass activity measurements) flow rates; the sequence of OCV, low current density, and high current density will be repeated until constant performance is reached.

Experimental materials in small single cells (4-50 cm<sup>2</sup>): ramp-in under voltage-control with a sequence of cycles consisting of 45 min. at 0.6 V followed by 5 min. at OCV and then by 10 min. at 0.85 V (i.e., 1 hour per cycle); the H<sub>2</sub>/air flow rates are kept constant at flow rates corresponding to a stoichiometry of 2/2 at a current density of 2 A/cm<sup>2</sup>. These one-hour cycles are repeated until constant performance is reached (ca. 6-8 cycles, i.e., for ca. 6-8 hours).

Further developed materials in short stacks: ramp-in under current-control with a sequence of cycles consisting of 45 min. at 0.8 A/cm<sup>2</sup> followed by 5 min. at OCV and then by 10 min. at 0.1 A/cm<sup>2</sup> (i.e., 1 hour per cycle); the H<sub>2</sub>/air flow rates are kept constant at flow rates corresponding to a stoichiometry of 2/2 at a current density of 2 A/cm<sup>2</sup>. If the single cell ramp-in (voltage-controlled, see above) with the same MEAs could not support 0.8 A/cm<sup>2</sup> at 0.6 V, then the high current density values in this current-controlled ramp-in will be reduced accordingly. These one-hour cycles are repeated until constant performance is reached (ca. 6-8 cycles, i.e., for ca. 6-8 hours).

Operation conditions for use in the new materials performance screening of CATAPULT MEAs:

Four characteristic polarisation curves per sample for 4-50 cm<sup>2</sup> single cell testing:

1. SAE (Society of Automotive Engineers) parameter standard polarisation curve leading in most cases to best MEA performance.
2. Humid: Evaluate the MEA under condensing conditions, this is important for evaluating the porous and surface nature of the pores within the electrode
3. Dry: Evaluate the MEA at low external humidification, this is important to evaluate the water retention and self-humidification of the MEA concepts.
4. Ideal Automotive: elevated operating temperature + reduced humidification
5. Oxygen reduction reaction mass activity (ORR MA) evaluation of new catalyst (support) materials.

Table 3. Test conditions for use in CATAPULT

The test protocols given in the previous version of the document have been reworked. The following table is giving a review of the new operating conditions as presented in the 12 months project meeting:

Again, these tests are obligatory only for a limited number of MEAs, being candidates for the downselection to the final MEA to be tested in an automotive single cell and short stack:

| ID                    | T <sub>Sample</sub> | RH <sub>A/C</sub>     | Pressure <sub>A/C</sub> | Stoichiometry <sub>A/K</sub> | Test type    |
|-----------------------|---------------------|-----------------------|-------------------------|------------------------------|--------------|
| SSK1                  | 80°C                | 100%/100%             | 1,7/1,7 bara            | 1,5/1,8                      | Polarisation |
| SSK2<br>(ORR MA test) | 80°C                | 100%/100%             | 1,7/1,7 bara            | 2,0/9,5                      | Polarisation |
| SSK3<br>(SAE)         | 80 °C               | 66%/66%               | 1,7/1,7 bara            | 1,5/1,8                      | Polarisation |
| SSK4<br>(dry)         | 80 °C               | 30%/30%<br>(TP 52°)   | 1,7/1,7 bara            | 1,5/1,8                      | Polarisation |
| SSK5<br>(humid)       | 50 °C               | 100%/100%<br>(TP 50°) | 1,7/1,7 bara            | 1,5/1,8                      | Polarisation |

Start with OCV, Reference cell: 50 cm<sup>2</sup> active area, Flowfield geometry: linear, Conditioning: 80°C/100 %

SSK1, SSK2, SSK3: obligatory test protocols for all CATAPULT MEAs

SSK4 & SSK5: additional test protocols for most promising MEAs (achieving > 80 % of performance targets)

SSK 1, 3: general performance evaluation

SSK 4, 5: evaluation of MEA operation robustness (behaviour in saturation conditions, behaviour in dry conditions)

SAE: Society of Automotive Engineers

Minimum hydrogen stoichiometry  $s = 2.0$  for cell sizes < 50 cm<sup>2</sup>

Start with =OCV

Project Performance targets: 0.65 V:  $\geq 1.2$  A/cm<sup>2</sup> (H<sub>2</sub>/air)

In order to be the most reproducible regarding fuel cell data acquisition, we propose a standard procedure for the measurement of H<sub>2</sub>/Air and H<sub>2</sub>/O<sub>2</sub> polarization curves in small single cells:

1. During the setting of the selected temperatures and pressures (see operating conditions in the above table), the cell is flushed with 500 sccm H<sub>2</sub>/Air or H<sub>2</sub>/O<sub>2</sub> (anode/cathode, respectively) and a constant cell voltage of 0.85 V is applied. Stoichiometric flows are adjusted once the pressures, temperatures, and dew points are reached.
2. A pre-acquisition condition is set prior to measuring the polarization curves by applying 0.75 V for 15 min at stoichiometric flow control (voltage-control mode), then switching to a current-control mode with a current density setpoint of 0.5 A/cm<sup>2</sup> for 15 min.
3. For the polarisation curves listed in Table 3, which are performed in a current-controlled mode, each current density point is held for 10 min. and the data are averaged over the last 10 seconds. The data acquisition sequence is the following:
  - a. H<sub>2</sub>/Air curves: Measurement @ 0.02; 0.05; 0.1; 0.2; 0.5; 0.8; 1; 1.2; 1.5; 1.7 A/cm<sup>2</sup> (10 min. each) and then OCV (3 min.).

- 
- b. H<sub>2</sub>/O<sub>2</sub> curves: Measurement @ 0.02; 0.05; 0.1; 0.2; 0.5; 1; 1.5 A/cm<sup>2</sup> (10 min. each) and then OCV (3 min.). This is the minimum number of points in order to get a correct Tafel plot for the oxygen reduction reaction.

## Durability evaluation of CATAPULT MEAs

Down-selected new catalyst materials and supports will be evaluated for stability in addition to the performance evaluation. In order to evaluate the susceptibility of different MEAs to degradation, a variety of different accelerated ageing tests are already available (JRC, DoE\*), each of which addresses a specific components of an MEA according to the expected degradation modes. CATAPULT will use the available protocols (Table 4) to assess catalyst and MEA performance stability on voltage cycling, and the stability of the catalyst support to potential hold.

Table 4. Accelerated stress test conditions for CATAPULT components and MEAs

| ID | specific | Scan range   | cycles | Anode | Cathode | Analysis | Conditions          | target   |
|----|----------|--------------|--------|-------|---------|----------|---------------------|--|
| 1  | catalyst | 0,6 to 1,0 V | 30.000 | H2    | N2      | CV, VIR  | 80°C, 100 kPa, 100% | ECSA: < 40% loss<br>VIR: < 30 mV loss (0,8 A/cm <sup>2</sup> )<br>j(mass): < 40% |
| 2  | support  | 1,5 V        | 24 h   | H2    | N2      | CV, VIR  | 80°C, 100 kPa, 100% | ECSA: < 40% loss<br>VIR: < 30 mV loss (1,5 A/cm <sup>2</sup> )<br>j(mass): < 40% |

Update modification to 2: max. voltage: 1,5 V, polarization curve every 1,2,4,8,16.... hrs.

These tests will be applied to the most promising MEAs developed within the project, according to the criteria given in 1.0.

\*)U.S. DRIVE Partnership, Cell Component Accelerated Stress Test and Polarization Curve Protocols for Polymer Electrolyte Membrane Fuel Cells, Revised December 16, 2010, ([http://www.uscar.org/commands/files\\_download.php?files\\_id=267](http://www.uscar.org/commands/files_download.php?files_id=267))

### Notes:

For the CATAPULT project the DoE protocol for catalyst (support) voltage-cycling stability (first line in Table 4) will be modified in order to simplify the data acquisition and to enable a better comparability for data acquired with different small scale hardware (active area, pressure drop, etc.):

- performance curves (U-I curves) will be recorded at the same intervals as ECSA measurements (cyclic voltammograms), namely before the first cycle and after 0.1k, 1k, 5k, 10k, 20k, and 30k cycles.
- polarisation curves will be recorded at a constant reactant inlet pressure of 150 kPaabs at 80 oC, 100%RH and stoichiometric H<sub>2</sub>/Air flows of 2/2 (this avoids major changes of operating conditions and thus is a more robust testing protocol). The procedures to prepare for acquisition of the polarisation curve and for measuring the polarization curve are identical to those outlined in the above discussion of Table 3.
- cyclic voltammograms are acquired at the same operating conditions using fully-humidified dilute hydrogen feed on the anode (5% H<sub>2</sub> in inert gas at 200 sccm) and nitrogen on the anode (flow rates corresponding to 1 sccm of N<sub>2</sub> per cm<sup>2</sup> of active area) at 20 mV/s.

Cell size: 5 – 50 cm<sup>2</sup> (50 cm<sup>2</sup> for the industrial partners).

### 1.2.2 MEA test protocols for zero-platinum electrocatalysts

Zero-platinum electro catalysts developed in the project will be tested in laboratory fuel cells 4-10 cm<sup>2</sup>, and 50 cm<sup>2</sup> cell for selected catalysts. While generally similar to the conditions used for Pt-based catalysts, distinct specificities of Fe-N-C or Co-N-C catalysts as well as short durability for the best performing ones till now requires some adjustments compared to the Pt MEA protocols.

For ORR mass activity measurement at 0.9 V, the conditions will be similar to entry 1 in Table 3 (under pure O<sub>2</sub> or air flow). H<sub>2</sub> cross-over effects combined with a Tafel kinetics restricted to a narrow range of currents for such catalysts implies that a thicker membrane (Nafion-117) is preferable for ORR mass activity measurement. A catalyst loading of 1 mg cm<sup>-2</sup> (mostly, corresponding to a mass of carbon and nitrogen, and a few wt % metal) will be used for this measurement. The loading of 1 mg cm<sup>-2</sup> (ca 25 μm thick active layer) lies on the lower end for non-PGM catalysts, but enables one to use the transfer decal method used for 50 cm<sup>2</sup> MEAs.

For initial power performance of non-PGM catalysts, the thin reinforced membrane chosen for Pt electrocatalysts will be used, in combination with a higher cathode catalyst loading of 3 mg cm<sup>-2</sup>. The latter is near the optimised loading observed so far for Fe(Co)-N-C catalysts tested under air or pure oxygen. No standard Nafion-to-catalyst mass ratio can be suggested, since this factor is catalyst-dependent, with huge variations of the total specific area and pore size distribution among various non-PGM catalysts.

### **Break in process and initial activity**

The operating conditions for break-in procedure are 80°C, 100%RH, 150 kPa<sub>abs</sub> gas inlet pressure and constant hydrogen/air (or O<sub>2</sub>) flow rates. The cell is let at open circuit voltage until the set temperatures and humidities have been reached. Two initial polarisation curves are recorded at 10 mV s<sup>-1</sup> from OCV down to 0.3 V, and then reversed. This fast measurement allows measurement of the polarisation curve without degradation of the catalyst. The cell is then potentiostatically controlled at 0.5 V until the current stabilized (in case of increased current with time) and a second polarisation from OCV to 0.3 V and then reversed scan, is measured.

### **Robustness evaluation**

The conditions identified in Table 3 can be applied to selected non-PGM catalysts, with a potentiostatic scan instead of a galvanostatic one, as specified in the break in process for non-PGM catalysts.

### **Durability evaluation**

Measurement of the ECSA as specified in entry 1 of Table 4 is impossible for non-PGM catalysts since the ORR active sites do not yield any electrochemical feature in a cyclic voltammogram. The double layer capacitance may however indicate changes in the total carbonaceous surface area. Measurement of the polarisation curve under O<sub>2</sub>/H<sub>2</sub> before and after cycling at 0.6-1.0 V vs. RHE will indicate the loss in mass activity, as for Pt-based catalysts. A total number of 10,000 cycles is suggested, with respect to the less mature level of non-PGM catalysts as compared to Pt.

The "catalyst support" test (entry 3 of Table 4) is not appropriate for carbon-based non PGM catalysts since voltages above 1 V are crippling the performance very rapidly due to carbon oxidation. System based solutions will be necessary to avoid this practical issue related to start/stop conditions, if non-PGM catalysts meet the other criteria of activity and of durability in stationary conditions.

## 2. *In situ* analytical methods

Beside performance and operating condition evaluation by polarisation curves it is necessary to get further data enabling more profound insight in the reaction zone of a MEA therefore it is necessary to combine measurements, especially in the process of an accelerated ageing test. Table 5 provides DoE and EU test specifications (Table 5) for cyclic voltammetry:

Table 5.

### **CV (DoE\*)**

0,05 - 0,60 V vs. RHE, 20 mV/s, 80°C, 100% RH

### **CV (EU°)**

Cathode and anode, 50 mV/s, 0,05 - 0,80 V, min. 3 cycles

### **Shorting**

#### **resistance (DoE\*)**

At 0,5 V, 80°C, 100 % RH, N<sub>2</sub>/N<sub>2</sub>, compression = 20 % strain GDL

### **Shorting**

#### **resistance (EU°)**

At 0,5 V, 80°C, 100 % RH, N<sub>2</sub>/N<sub>2</sub>, compression = 20 % strain GDL

### **H<sub>2</sub>-cross (EU°)**

At 0,42 V, p(H<sub>2</sub>) = 1,5 bar / p(N<sub>2</sub>) = 1 bar, full RH, 80°C

4 mV/s, 0,05 - 0,80 V, 1 cycle

### 3. Component analysis

Table 6 below outlines techniques that are available to partners to characterise MEA components. It will be used selectively to help interpretation of the cell test data obtained from the CATAPULT components.

Table 6. Techniques and characterisation methods available for CATAPULT components

| Component                  | Test                             | Information Obtained  | Partner      |
|----------------------------|----------------------------------|---|--------------|
| <b>Catalyst</b>            |                                  |   |              |
|                            | CO Metal Area                    | Gas phase accessible metal area   | JM, UM2      |
|                            | Nitrogen sorption                | BET surface area, micropore pore size distribution                        | JM, UM2, TUM |
|                            | Wet cell electrochemical cycling | Stability of catalyst to voltage cycling in an acidic environment         | JM, UM2      |
|                            | Rotating disk electrode          | Mass and specific activity  | JM, UM2, TUM |
| <b>Catalyst layer</b>      |                                  |   |              |
|                            | Mercury porosimetry              | Porosity and pore size distribution                                       | JM, UM2      |
|                            | Dynamic Vapour Sorption          | Water vapour uptake rate  | JM, UM2      |
| <b>Gas diffusion layer</b> |                                  |   |              |
|                            | Conductivity                     | Through plane and in-plane conductivity                                   | JM           |
|                            | Mechanical testing               | Compressibility and resistance to bending                                 | JM           |
|                            | Mercury porosimetry              | Pore size distribution (including microporous layer)                      | JM           |
|                            | Water porosimetry                | Capillary pressure curve (excluding microporous layer)                    | JM           |
|                            | Nitrogen sorption                | BET surface area. Micropore distribution (dominated by microporous layer) | JM           |
|                            | Dyne ink                         | Superficial surface energy of microporous layer                           | JM           |
| <b>Membrane</b>            |                                  |   |              |
|                            | Water Permeability               | Relative rate of water transport across membrane                          | JM, VTT      |
|                            | Dimensional Stability            | Amount of swelling when membrane exposed to hot water                     | JM, UM2      |
|                            | Mechanical testing               | Tensile properties and tear resistance at 23°C 50% RH                     | JM, UM2      |
|                            | Thermomechanical                 | Softening temperature   | JM           |

|                  |   |  |          |
|------------------|---|--|----------|
|                  | Analysers   |  |          |
|                  | Proton conductivity   | Conductivity at various temperatures and relative humidities | UM2      |
| Catalyst support |   |  |          |
|                  | Electronic conductivity, via in-plane resistance measurements, four point measurement | Conductivity at various temperatures                         | UM2, VTT |
|                  | Through plane resistance measurements, four point measurement                         | Conductivity   | VTT      |
|                  | Nitrogen sorption/desorption  | BET surface area, pore size distribution                     | UM2      |
|                  | Wet cell electrochemical hold   | Electrochemical corrosion resistance of support at 1.2 V     | UM2, VTT |
|                  | XPS, XRD, XRF   | X-ray methods for compositional analysis                     | UM2      |
|                  |   |  |          |

Table 7 gives an overview on test methods available at the partners. The intention is to enable materials developed within the project to be tested by the partners, if relevant methods are available:

Table 7. Test methods available for CATAPULT components

| Method                           | UM2 | TUM | JMFC | BQ | UULM | VTT | VW |
|----------------------------------|-----|-----|------|----|------|-----|----|
| CV                               | X   | X   | X    |    | X    | X   | X  |
| Impedance                        | X   | X   | X    |    | X    | X   | X  |
| FC Test Stands                   | X   | X   | X    |    |      | (X) | X  |
| Digital Microscope               | X   | X   | X    |    |      | X   | X  |
| Scanning Electron Microscopy-EDS | X   | X   |      |    | X    | X   |    |
| Water balance                    |     |     | X    |    |      |     |    |
| Cell reversal                    |     | X   | X    |    |      |     |    |
| Anode and cathode corrosion      |     |     | X    |    |      |     |    |
| single cell start/stop testing   |     | X   |      |    |      |     |    |
| TGA/DSC + MS                     |     |     |      |    |      | X   |    |

### 3.1 Experimental protocols

#### **3.1.1 Catalyst support evaluation:**

First selection criteria for support evaluation are electronic conductivity, surface area and resistance to corrosion.

#### **Out-of-cell studies**

Surface area will be determined by BET ( $N_2$  adsorption-desorption analysis). Electronic conductivity measurements of the new catalyst supports will be carried out at temperature between ambient and 100 °C on a pellet prepared with the support powder obtained at moderate compaction pressures (10, 20 kg  $cm^{-2}$ ) similar to those used for MEA hot-pressing and single cell assembling (compression).

#### **Support stability testing in half cell with reference liquid electrolyte:**

These experiments will serve as a screening to compare the electrochemical degradation in an acidic environment of different supports. The electrolyte is sulfuric acid 0.5 M and the temperature is 80 °C. The liquid electrolyte will provide a proper environment in terms of water content and proton activity and these experiments are useful to predict the level of corrosion in PEMFC. The effect of temperature on support corrosion will also be investigated at the catalyst level under single cell PEMFC operation. Since the corrosion of benchmark carbon black supports is the main driving force of catalyst degradation, it is appropriate to quantify the corrosion in terms of loss of material by electrochemical oxidation (accelerated experiments) at 1.2 V RHE for 24 h or 1.4 V RHE for 2 h. The first condition represents the thermodynamic potential limit of PEMFC operation under normal condition; the latter condition may be appropriate to provide information on corrosion under starvation or unusual operation conditions. Support degradation will be estimated in terms of loss/modification of support from the integrated corrosion current.

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

#### **3.1.2 Catalyst evaluation by RDE**

For platinum based catalysts, Rotating (ring) disc electrode measurements will be employed to evaluate new catalysts (promising catalysts will subsequently be tested in MEAs); catalysts will be attached onto a glassy carbon disk using Nafion binder. 0.1 M  $HClO_4$  (or 0.1 M  $H_2SO_4$  for non-PGM catalysts, no adsorbing effect) at 60°C will be used as electrolyte in a thermostated three-electrode two-compartment cell, whereby the reference electrode (Ag/AgCl) is calibrated to the RHE scale by measuring the  $H_2$  oxidation/evolution potential at zero current on the platinum ring electrode. Electrochemical surface area (ECSA) as well as mass ( $i_m$ ) and specific activity ( $i_s$ ) at 0.9  $V_{RHE}$  of the catalyst can be quickly determined. For break-in of Pt-based catalysts, 50 cyclic voltammograms in de-aerated, argon saturated electrolyte are recorded between 0.05  $V_{RHE}$  and 1.2  $V_{RHE}$  at a scan rate of 50 mV/s. ECSA is determined from the 50<sup>th</sup> cycle. After saturating the electrolyte for 15 min with oxygen, 5 cycles from 0.05  $V_{RHE}$  to 1.0  $V_{RHE}$  are recorded at a rotation rate of 1600 rpm and at 50 mV/s; subsequently, 3 cycles are recorded at 5 mV/s. The ring is meanwhile held at 1.2  $V_{RHE}$  to quantify the amount of hydrogen peroxide.  $i_m$  and  $i_s$  are determined from the 3<sup>rd</sup> positive-going scan at 5 mV/s after  $iR$ -correction.

For non-PGM catalysts, catalysts will be attached onto a glassy carbon disk using Nafion binder. 0.1 M  $HClO_4$  (or 0.1 M  $H_2SO_4$ , no adsorbing effect) at 60°C will be used as electrolyte in a thermostated three-electrode two-compartment cell, whereby the reference electrode (Ag/AgCl) is calibrated to the RHE scale by measuring the  $H_2$  oxidation/evolution potential at zero current on the platinum ring electrode;

or by using a direct RHE electrode. For break-in of non-PGM catalysts, 2 cyclic voltammograms in O<sub>2</sub>-saturated electrolyte are recorded between 0.05 V<sub>RHE</sub> and 1.0 V<sub>RHE</sub> at a rotation rate of 1600 rpm and at 5 mV/s. The electrolyte is then saturated with N<sub>2</sub> for 15 min, and a minimum of 3 cycles at 5 mV/s are recorded. The mass activity can be determined in positive or negative going scans.