NEXT GENERATION PEM ELECTROLYSERS UNDER NEW EXTREMES

HORIZON 2020 PROGRAMME

FUEL CELLS AND HYDROGEN JOINT UNDERTAKING (FCH 2 JU)

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DELIVERABLE REPORT

D5.1 – ASSESSMENT OF MEMBRANE ELECTRODE ASSEMBLIES FOR HIGH TEMPERATURE AND HIGH-PRESSURE OPERATION	
Due Date	31-July-2019
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DISSEMINATION LEVEL		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	

Summary	
Keywords	Electrolysis, Polymer electrolyte membranes, MEAs, high temperature and pressure, high efficiency
Abstract	The NEPTUNE project develops a set of breakthrough solutions at materials, stack and system level to operate at high temperature (90-140ºC) and high nominal current density (4 A·cm^{-2}), while keeping the energy consumption <50 kWh/kg H_2 and directly produce hydrogen at 100 bars. The relative high stack temperature is managed by using an Aquivion® membrane. The aimed high efficiency at elevated current density is realised using a 50 µm thin reinforced Aquivion® membrane, able to withstand high differential pressures. The gas crossover is safely managed by adding an efficient recombination catalyst. Improved electrocatalysts with high activity and stability has been developed. The developed improved precursors have allowed the manufacture of well performing MEAs with ultralow catalyst loadings (0.44 mg$_{PGM}$/cm^2). MEAs added 0.2 mg recombination catalyst per cm^2 fulfils the ambiguous NEPTUNE performance targets of $\leq$1.75 V at base load (4 A/cm^2) and $\leq$2.2 V at peak load (8 A/cm^2). Furthermore, degradation rates ≈5 µV/h are measured for these ultralow PGM loaded MEAs.
Public abstract for confidential deliverables	N.A. - Public Deliverable

CO	Confidential, only for members of the consortium (including the Commission Services)	
Nature of the Deliverable		
R	Report	**X**
D	Demonstrator	
O	Other	

Revisions

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0.1	18-07-209	Laila Grahl-Madsen	
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D5.1 – Assessment of membrane electrode assemblies for high temperature and high-pressure operation

Acronym table

Abbreviation	Explanation
BET	Brunauer–Emmett–Teller
CAPEX	Capital expenditures
CCM	Catalyst Coated Membrane
EW	Equivalent Weight
FC	Fuel Cell
GDL	Gas Diffusion Layer
HHV	Higher Heating Value
MEA	Membrane Electrode Assembly
PEM	Proton Exchange Membrane
PFSA	PerFluoroSulfonic Acid
PGM	Platinum-Group Metals
RC	Recombination Catalyst

1. Introduction

The main advantages of PEM electrolysis are the ability to produce ultrapure hydrogen at high pressure. Furthermore, PEM electrolysers is well suited for dynamic behaviour e.g. in connection with storing renewable electrical energy in hydrogen. The main disadvantage is related to the CAPEX cost that to a certain extend is related to the use of noble metals. The NEPTUNE approach to overcome this challenge is to develop ultralow PGM loaded MEAs that are capable to operate at high current density. The WP5 activities of NEPTUNE comprise the design of advanced membrane electrode assemblies (MEAs) for PEM electrolysis applications with the aim of improving performance and durability while simultaneously reducing cost. The WP also cover stack optimisation. However, this report solely concerns the development and characterization of the optimised PEM-electrolysis MEAs that are developed with the following project specific targets in mind:

- Use of thin cost effective short-side chain PFSA membranes
- Manufacture low PGM loaded MEAs with $\leq$0.4 mg_{PGM}/cm^2
- Demonstrate an efficiency of $E_{Cell} \leq 1.75$ V at 4 A/cm^2 (nominal operational point) and a short-term efficiency of $E_{Cell} \leq 2.2$ V at peak load of 8 A/cm^2
- Validate a long-lifetime potential; targeting a degradation rate of $\leq$5 µV/h/MEA at nominal operation conditions
- Ensure max 0.5% H_2 in the oxygen stream across the entire load curve; corresponding to max 1% loss of faradic efficiency
- Enable a high H_2 output pressure of 100 bar for current densities ranging between 0.2 and 8 A/cm^2
- Demonstrate that the produced hydrogen is ultrapure (>5N)

The starting point of the NEPTUNE MEA developing work was the encouraging results obtained in the *on-going* FCH JU project HPEM2Gas.[1] The MEA development and manufacturing processes were supported by *in-situ* and *ex-situ* methods for characterisation and testing of the inks, electrodes, and MEAs. Intensive exchange of information among the project partners enabled the improvement of components and leading to the first selection of materials and ink formulations.

2. Scope

This report summarises the results of the performed work at CNR-ITAE covering the development of the advanced NEPTUNE MEAs that fulfil the project targets outlined above.

3. Experimental

Details on the NEPTUNE membrane and the catalyst-precursor development is reported in the public NEPTUNE deliverable reports, D3.1[2] and D4.1[3] respectively. A list of the NEPTUNE CCM-precursors utilised for the MEA manufacture reported *ibid* is provided in Table 3.1.

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[1] http://hpem2gas.eu/

[2] http://www.neptune-pem.eu/images/PDF/D.3.1%20%E2%80%93%20Supply%20of%201st%20Generation%20Reinforced,%20Recast%20and%20Extruded%20Aquivion%C2%AE%20Membrane%20and%20Ionomer%20Dispersions%20for%20High%20Temperature%20and%20High%20Pressure%20Operation.pdf

[3] http://www.neptune-pem.eu/images/PDF/D4.1%20%E2%80%93%20Data-set%20on%20catalytic%20activity,%20electrochemical%20performance%20and%20stability%20of%20enhanced%20catalysts.pdf

Table 3.1 Utilised CCM precursors.

ID	Explanation	Comments
E98-05S	Solvay extruded baseline membrane	Aquivion® E98-05S is a chemically stabilized PFSA ionomer membrane with an EW of 980 g/eq. The E98-05S is 50 µm thick
D98-06ASX	Solvay ionomer	EW=980 g/eq, stabilized ionomer. Dispersion is formulated with propanols and have 6 wt% of polymer content
IrRuOx	CNR-ITAE anode catalyst	Nanostructured $Ir_{0.7}Ru_{0.3}O_X$ tetragonal anode catalysts with a core-shell configuration consisting of Ir enrichment on the surface and optimised crystallographic orientation. The crystallite size ≈8 nm and the specific surface (BET) ≈160 m^2/g
Pt/C	CNR-ITAE cathode catalyst	40 wt% Pt on carbon; crystallite size ≈3 nm; specific surface area 47 m^2/g (BET)
PtCo	CNR-ITAE recombination catalyst	Nanostructured cubic $Pt_{5.6}Co$ recombination catalyst with a core-shell configuration consisting of Pt-enriched surface and a crystallite size of 4 nm

All CCMs are design symmetrically with respect to type of ionomer. The catalyst inks were directly sprayed onto the membranes. Carbon GDL was applied to the cathode.

Single cell hardware for the initial screening of various combinations of electrocatalysts and ionomers differ in terms of active area (3-8 cm^2) and/or operating mode e.g. pressurised or ambient pressure operation. The actual test conditions temperature, pressure etc. are listed together with the individual presented results. The MEAs were tested with Type I DI water (18.2 MΩ·cm) supply to the anode and no cathode water supply. The anode water is recirculating in the single cell test; the water was maintained at the cell temperature. Electrochemical measurements include polarization curves, electrochemical impedance spectroscopy (EIS), galvanostatic durability tests. Hydrogen concentration in the oxygen stream was monitored by an AGILENT micro GC. The presented results are obtained at CNR-ITAE.

4. Results and Discussion

Optimisation of NEPTUNE precursors (Table 3.1), ink composition and MEA manufacture has resulted in well performing MEAs. The performance at various temperatures of such an ultralow PGM-loaded MEA is shown in Fig. 4.1. The specific cell potentials at the NEPTUNE target current densities is listed in Table 4.1. The project target performance is reached for 8 A/cm^2 at 90ºC, and only 50 mV higher than the target performance at 4 A/cm^2.

No or very little negative influence of the ultralow PGM-loaded MEAs are noted in the *on-going* long-term steady state test at 4 A/cm^2 (Fig. 4.2). The degradation rate is calculated disregarding the first 900 test hours as voltage losses here are mainly marked by reversible losses. The recorded voltage loss over the last 2,500 hours at 4 A/cm^2 is 5.1 µV/h.

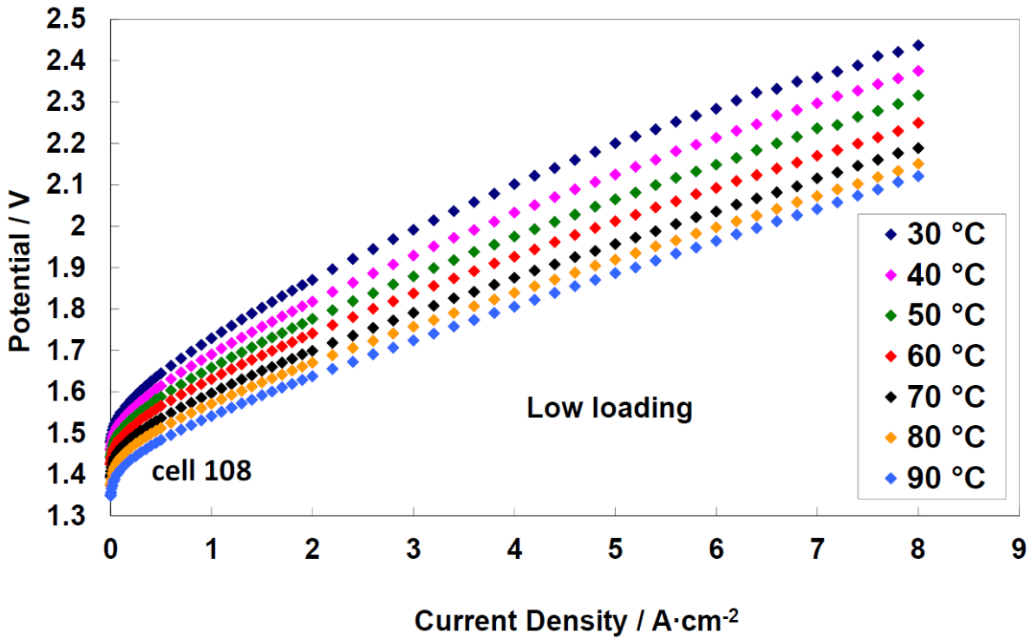

Fig. 4.1 Performance of an optimised MEA at ambient pressure. The MEA is based on E98-05S, and with the PGM-loading of 0.34 $mg_{Ir0.7Ru0.3}/cm^2$ and 0.1 mg_{Pt}/cm^2.

Table 4.1 List of obtained performance at target current density for a MEA based on E98-05S, and with the PGM-loading of 0.34 $mg_{Ir0.7Ru0.3}/cm^2$ and 0.1 mg_{Pt}/cm^2 cf. Fig. 4.1.

T [ºC]	E_{Cell} @ 4 A/cm^2	E_{Cell} @ 8 A/cm^2
70	1.87	2.18
80	1.83	2.15
90	1.80	2.12
NEPTUNE Target @ 90-140ºC	1.75	2.2

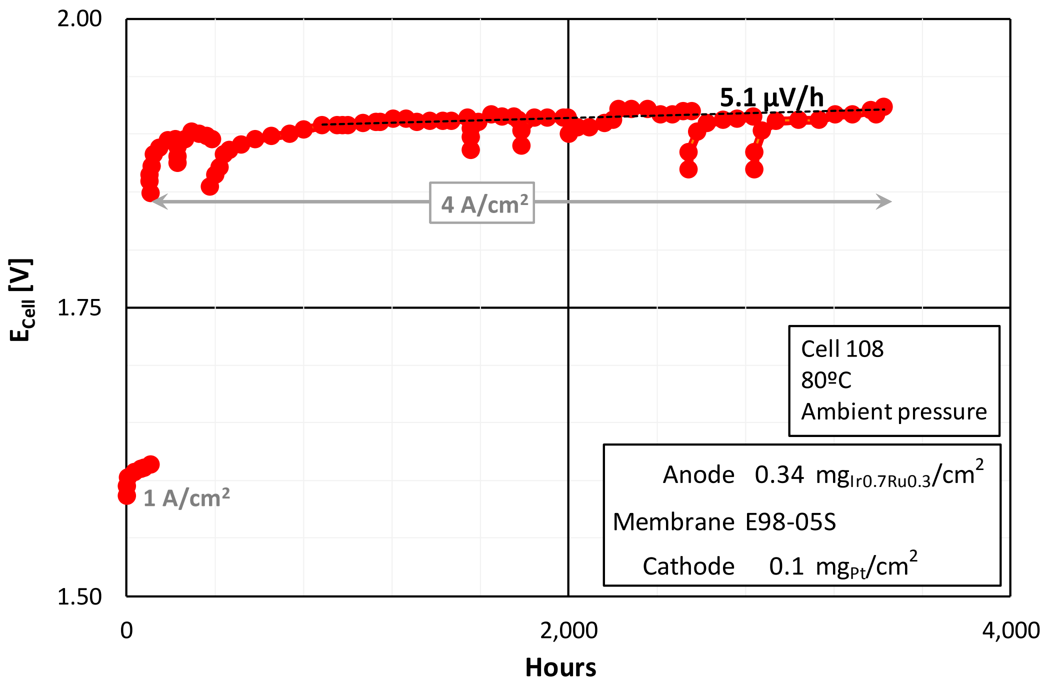

Fig. 4.2
Steady state long-term test of an ultralow PGM loaded MEA.

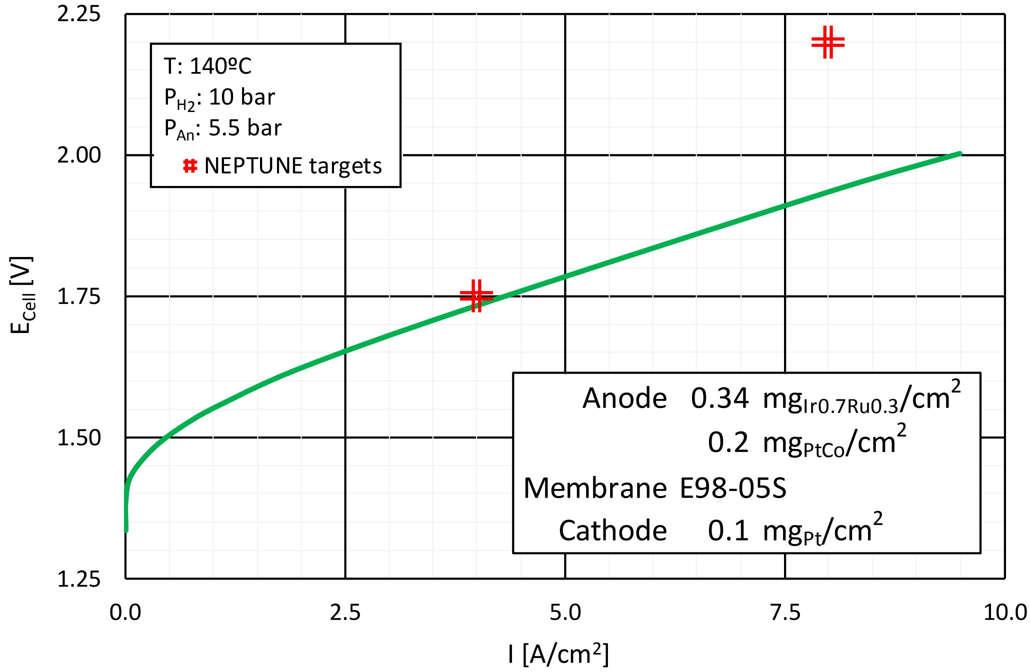

Fig. 4.3
Performance of an optimised MEA with RC at 140 °C.

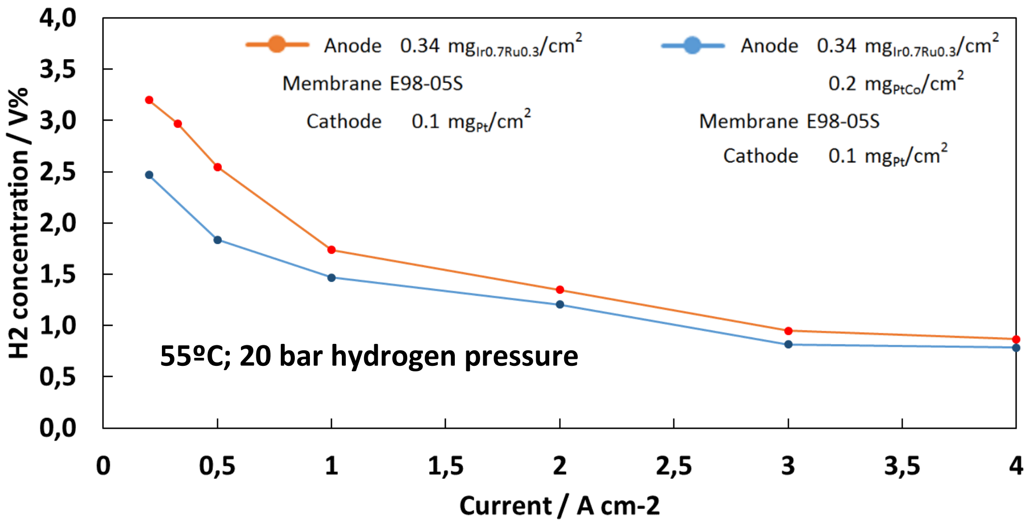

Fig. 4.4 Measured hydrogen crossover.

The use of a thin membrane (50 µm cf. Table 3.1) do explain some of the impressive obtained performances of the ultralow PGM-loaded MEAs. However, a thin membrane not only reduce the resistance (improve performance) but will also enhance the hydrogen crossover compared to MEAs based on a thicker membrane. Various recombination catalysts (RC) has been investigated. The addition of 0.2 mg$_{PtCo}$/cm^2 to the anode not only improved the performance (Fig. 4.3), but also showed a good capability of reducing the hydrogen concentration in the oxygen stream well below the Lower Explosion Limit of 4% (Fig. 4.4 & 4.5). The MEA with RC added to the anode show a rather constant hydrogen crossover at 140°C that is lower than the crossover recorded below 2 A/cm^2 at 55 and 90ºC, but higher above 2 A/cm^2 at 55 and 90ºC. The increased oxygen pressure at the anode in the experiment at 140°C can provide a barrier to the hydrogen permeation and at the same time promote the recombination process at the recombination catalyst surface especially at low current densities when the hydrogen permeation rate is low. Similarly, the increased operation temperature (140°C) can also promote the recombination process at recombination catalyst surface. Both mechanisms produce a drastic change of the hydrogen concentration in the oxygen stream at high temperatures and low currents.

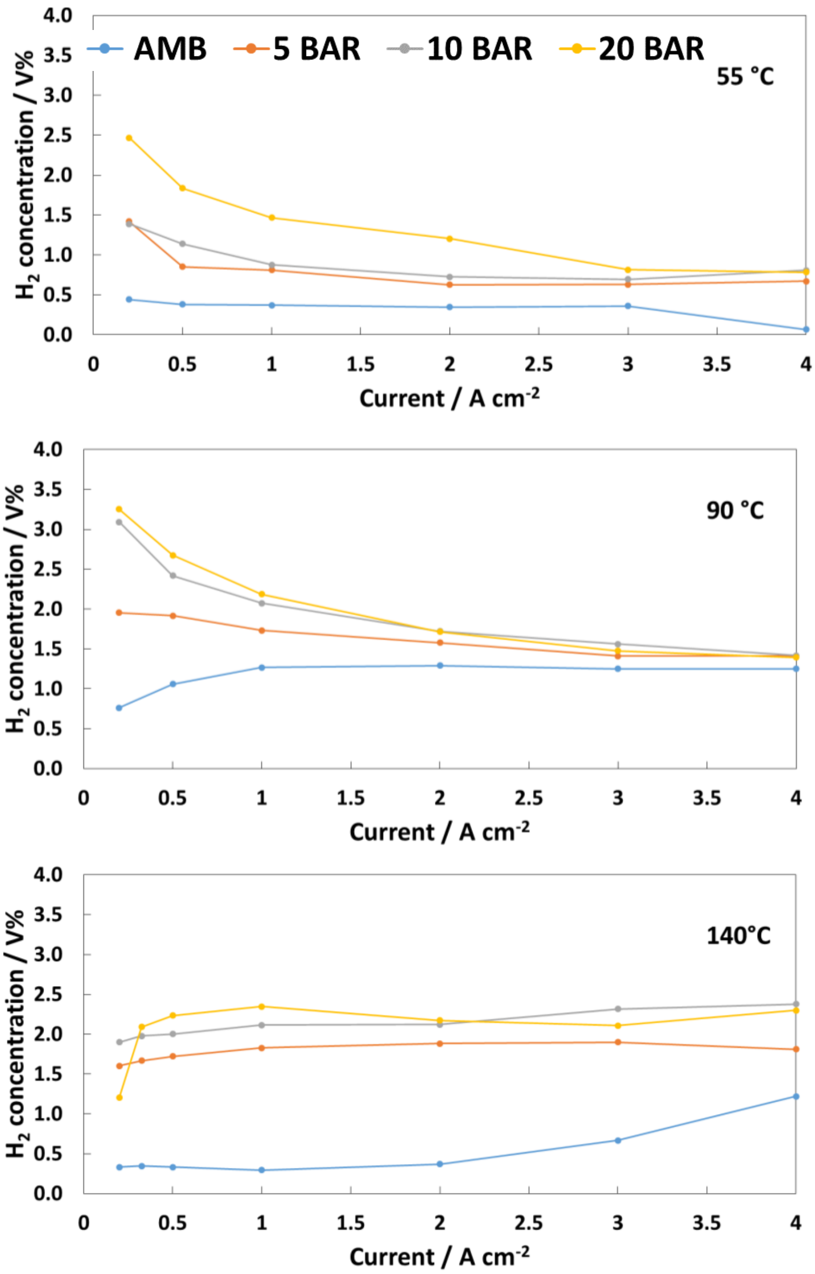

Fig. 4.5
Hydrogen crossover at different temperature and hydrogen pressure. The anode pressure at 140ºC is 5.5 bar(abs).

5. Conclusions

The MEA development done at CNR-ITAE, using the optimised NEPTUNE precursors has successfully demonstrated that:

- The NEPTUNE MEA performance targets are almost obtained for ultralow loaded (0.44 mg_{PGM}/cm^2) MEAs at base load 4 A/cm^2 and 90ºC (goal 1.75 V, obtained 1.80 V). The peak load (8 A/cm^2) performance target is obtained with this ultralow loaded MEA; peak target performance 2.2 V, obtained performance 2.12 V
- The steady state voltage loss at base load is 5.1 µV/h over the last 2,500 test hours
- It is possible to mitigate a high hydrogen crossover due to the use of a thin membrane by adding 0.2 mg_{RC}/cm^2 to the anode catalyst layer
- The ambiguous NEPTUNE performance targets are obtained for a MEA with 0.2 mg_{RC}/cm^2 in the anode catalyst layer (in total 0.63 mg_{PGM}/cm^2) at 140ºC, proven performance is 1.73 V @ 4 A/cm^2 and 1.93 V @ 8 A/cm^2