Memo

2012-12-19

To	Partners in the NEXPEL project
Copy	Børre Tore Børresen Oddmund Wallevik
From	Stein Trygve Briskeby
Subject	**Deliverable 4.2 MEA tested with UoR membrane under different operating conditions**

1 Introduction

This memo reports the results obtained within the NEXPEL consortium on the use of SPEEK membranes in membrane electrode assemblies/catalyst coated membranes (MEA/CCM). Three partners have been involved in this work, CEA, SINTEF, and FuMA-Tech. The main conclusions from the work are summarized in this memo. For more details, the reader is referred to the reports from the individual partners, which can be found as Appendixes 1 – 3.

2 Experiments and results

2.1 Experiments at CEA

- SPEEK membranes from UoR were tested for H2 permeation by electrochemical measurements. The obtained permeation values at 25°C were close to values obtained for Nafion ® 115, which is considered as a good result given that the SPEEK membrane is considerably thinner than Nafion ® 115 (142µm vs. 40 µm). It is noted that permeation normally increases with temperature; a doubling is typical for Nafion going from 25 to 80°C.
- Four MEAs were prepared by direct spraying on the membrane (1 pcs) or decal transfer by hot-pressing (3 pcs). Direct spraying resulted in delamination when immersing the MEA in water. Adherence was sufficient for the decal method. However, the membrane was easily damaged during hot-pressing.
- Two of hot pressed MEAs were tested electrochemically (MEA 2 and MEA 3). The results are given in the table below.

	E @ 1 A cm^{-2} (60°C) /V	E @ 1 A cm^{-2} (80°C) /V
MEA2	1.733	1.684
MEA3	1.86	-

MEA2 was run for 60 h before the gas purity H2 in O2 reached 2% and the experiment stopped. MEA3 was run for 60 h at 60°C with now increase in H2 in O2 (constant at 0.6 %). However, when temperature was raised to 80°C, the H2 in O2 concentration increased, and holes where found in the membrane during dissembling of the cell.

2.2 Experiments at SINTEF

- SPEEK membranes developed by UoR and casted by FuMA-Tech were coated with Ir/ATO catalyst by spraying of a catalyst ink with Nafion as binder. The prepared MEA had an anode catalyst loading of 1 mg Ir/cm^2. A standard E-TEK gas diffusion electrode with a Pt loading of 0.5 mg/cm^2 was used as cathode.
- Electrochemical measurements were performed at 60°C. Polarization curves were recorded at t=0, 10 and 20 h with operation at 1.7 V in between. The cell was then heated to 80°C and a new polarization curve was recorded. After 4 h at 1.7 V the cell shut down after membrane failure.
- Cell performances of ~1.7 V and ~1.6 V @ 1 A cm^{-2} at temperatures of respectively 60°C and 80°C was achieved with cell resistances comparable or lower than state-of-the-art PEM electrolyser MEAs.
- The tests showed that it is, without any major changes in the manufacturing process, possible to make catalyst coated membranes with the sPEEK membrane made by UoR/FuMA-Tech. The mechanical stability could be improved by reinforcing the whole membrane or adding an edge reinforcement film.

2.3 Experiments at FuMA-Tech

- Coating experiments with SPEEK membranes and different ink compositions were performed. Utilizing SPEEK material as polymer and binder was unsuccessful resulting in delamination of the catalysts layer. Better results were achieved with PFSA as ionomer, but due to swelling of the membrane, very thick inks challenging the limits of process ability in the coating device had to be utilized. By this method catalyst coated membranes (CCM) were successfully prepared.
- Three CCMs were prepared for electrochemical testing. Due to poor mechanical stability all CCMs broke during assembling of the cell, and no measurements could be made.

3 Conclusions

- MEAs/CCMs with SPEEK membrane material from UoR/FuMA-Tech can be prepared with reasonable performance and conductivity. The stability proved to be poor and needs to be significantly improved for future use in PEM electrolysis.
- Adhesion of catalyst material is challenging and could be achieved by using PFSA type ionomers as binders in the ink. SPEEK ionomers as binders proved to be difficult.
- The material is fragile, and reinforcement is necessary for improving mechanical stability and lifetime.

Appendix 1: CEA - Results of water electrolysis tests obtained for MEA composed of SPEEK membrane synthesized at University of Reading

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Electrolyseurs et de Modélisation

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« NEXPEL Project »
Next-generation PEM electrolyzer for sustainable hydrogen production

Results of water electrolysis tests obtained for MEA composed of SPEEK membrane synthesized at University of Reading

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LISTE DE DIFFUSION

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Sommaire

I. Introduction

This report present the main results obtained in water electrolysis tests of membrane electrode assemblies (MEA) composed of a SPEEK membrane synthesized at the University of Reading (UoR) in the frame of the NEXPEL project.

II. The Membrane Electrode Assemblies

II.1 Characterizations of the membrane

Nafion® 115 (127 µm) is taken as a reference.

Thickness of the membrane

25°C	N115	SEEK UoR
Dry thickness	127 µm	40
Wet thickness	142 µm	42
Swelling (%)	11.8 %	5 %

Permeation measurements at 25°C :

Linear Sweep Voltammetry could be used to measure the cross over of hydrogen through the membrane.

Principle

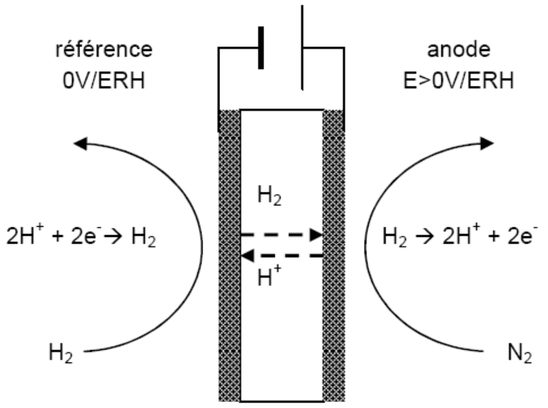

Figure 1: principle of the measurement

For the measurement, two gas diffusion electrodes (GDE, carbon paper + carbon supported platinum) are placed on each sides of the membrane (simple contact). The counter electrode is used as the reference. This electrode is considered as a reversible hydrogen electrode (RHE) since a flow of hydrogen (30 ml min^{-1}) is sent to the platinum electrode. The working electrode is inerted by nitrogen flow (50 ml min^{-1}). The potential of the working electrode is swept between 50 mV *vs.* RHE and 0.9 V *vs.* RHE. In order to obtain a steady state the scan is usually run very slowly typically 4 mV s^{-1}. At the working electrode, the hydrogen present from the cross over is oxidized (with a sufficient overvoltage). This current of oxidation is used to measure the flow of permeation as:

$$\Phi = \frac{I_{\lim}}{2\,FS}$$

Φ : hydrogen flow en mol s^{-1} cm^{-2}

I_{lim} : current of oxidation (at 0.6 V *vs.* RHE)

F : Faraday constant (96500C.mol^{-1})

S : electrode surface area (cm²)

Measurements were realised for the SPEEK membrane placed in a cell of 25 cm². The wet and dry membrane was tested. Values measured in a French project (AIRELLES, PAN'H 2008) for N115 are given comparatively.

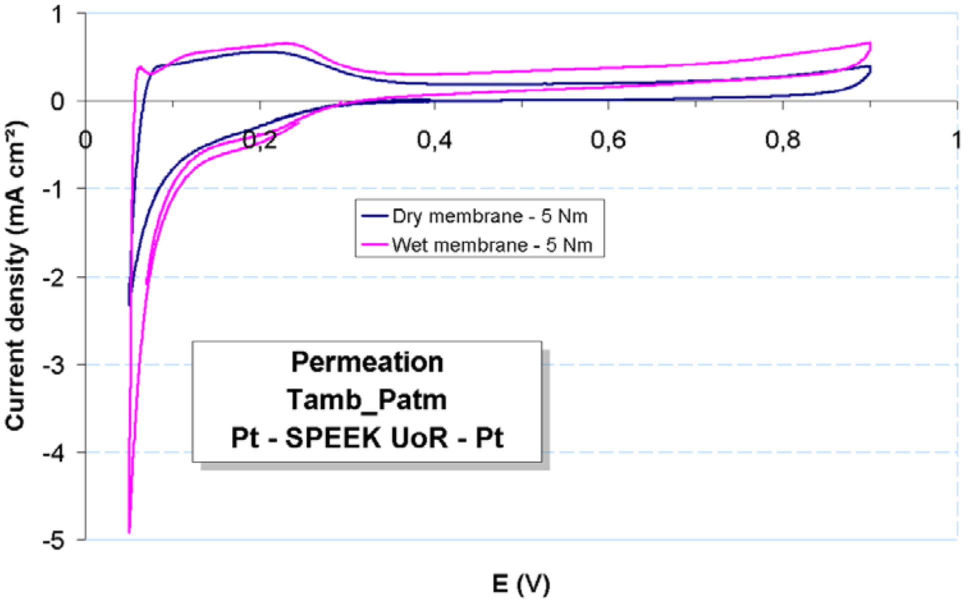

Figure 2: LSV at 25 °C obtained for SPEEK membrane

The permeation of hydrogen is higher for the wet membrane as generally observed.

25°C	N115	SEEK UoR dry	SEEK UoR wet
J_{lim} (mA cm^{-2})	0.226	0.17	0.269
Flow (mol_{H2} s^{-1} cm^{-2})	1.170E-09	0.808E-09	1.394E-09
H_2 Flow (ml h^{-1})	2.4	1.8	2.9

Values of permeation obtained for the SPEEK membrane are close to the values obtained for a Nafion® 115 membrane. These results are interesting considering an important difference of thickness between N115 (142 µm) and wet SPEEK (40 µm).

At 1 A cm^{-2} for a surface area of 25 cm², the oxygen production is around 5.2 l h^{-1}. If we consider a flow of hydrogen in oxygen of around 2.9 ml h^{-1}, the rate of hydrogen in oxygen should be **0.055 %.**

Nevertheless, it is important to specify that these measurements were performed at 25°C. The gas permeation is higher when the temperature increases as presented in the table below for the Nafion 115 (twice higher).

H_2 permeability (mol_{H2}.cm.s^{-1}.cm^{-2}.Pa^{-1})	N115
25°C	1.645E-16
80°C	2.915E-16

As the electrolysis tests are performed at 60°C, values of permeation could be higher. Besides, the clamping of the MEA in a cell could influence the cross over and have to be considered (micro holes…).

II.2 Preparation of the MEA

Membrane Electrode Assembly were prepared by direct “catalyst coated membrane” (CCM) or by transfer of electrocatalytic layers. In direct, CCM, inks of catalysts are sprayed or printed directly in the membrane. In “transfer method”, inks are first deposed in a neutral support and second transferred on the membrane by hot pressing as shown below.

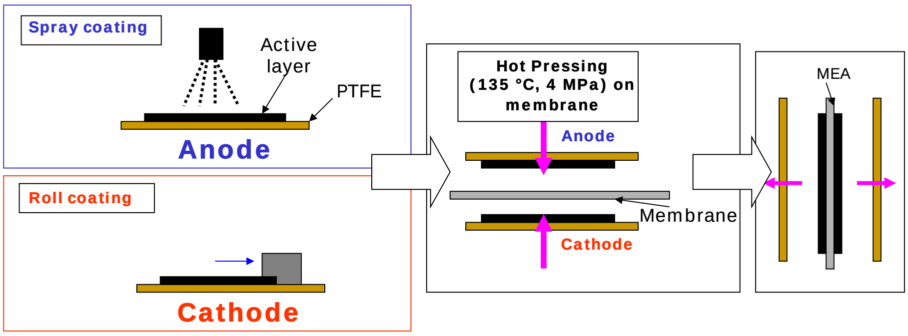

Figure 3: transfer method to synthesize MEA

The binder of inks is generally a suspension of Nafion. However, here the membrane is composed of SPEEK. Consequently, the interface is not perfect. In the case of direct CCM, the MEA delaminate when it was put in water before the cell test. The adherence was probably not sufficient. The preparation by transfer was the most interesting.

II.3 MEA tested

The compositions of the MEA synthesized at CEA are given in the table below:

N°	Ref CEA	Anode	Membrane	Cathode	Synthesis
1	180	$IrO2$ 1,49 mg cm^{-2}	SPEEK UoR	Pt 0,21 mg cm^{-2}	CCM
2	182	$IrO2$ 1,49 mg cm^{-2}	SPEEK UoR	Pt 0,22 mg cm^{-2}	Transfer
3	194	$IrO2$ 2,9 mg cm^{-2}	SPEEK UoR	Pt 0,23 mg cm^{-2}	Transfer
4	195	$IrO2$ 3,2 mg cm^{-2}	SPEEK UoR	Pt 0,23 mg cm^{-2}	Transfer

NB : Electrocatalytic layers of the MEA n°1 realized by CCM delaminated and the test was not possible.

The MEA n°4 was degraded during the clamping of the cell. Consequently, the presence of big holes could not allow beginning the test (very high permeation).

III. MEA n°2

III.1 Performances

The conditioning protocol is a sequence of increase/decrease of current density from 0.2 A cm^{-2} to 2 A cm^{-2} during around 15 h.

Electrical performances obtained at 60 and 80°C are presented below:

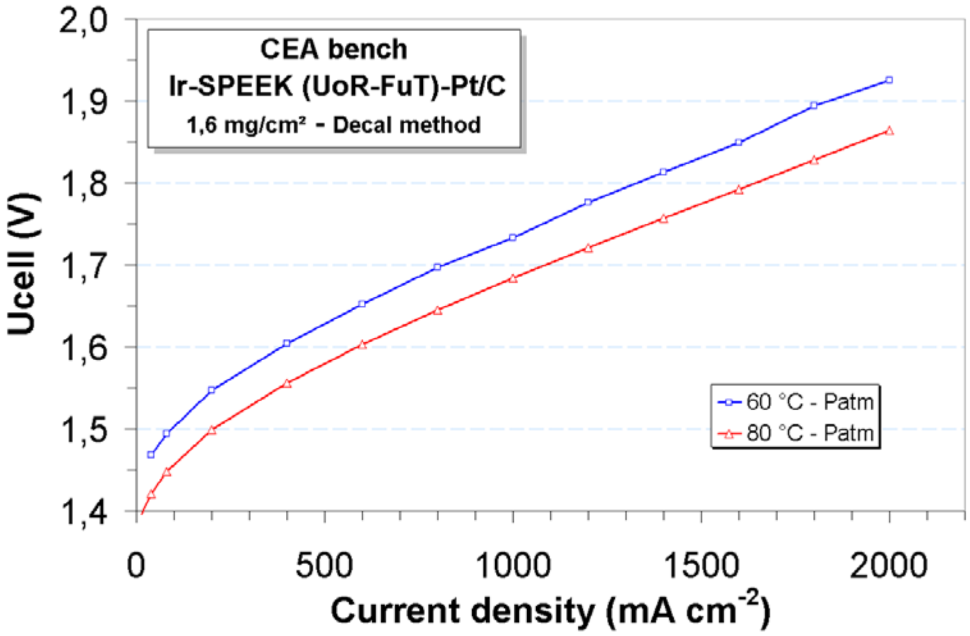

Figure 4: Polarization curves at 60°C and 80°C - Patm obtained for the MEA n°2

The electrical performances obtained for this water electrolysis monocell test are very interesting with **1,733 and 1,684 V at 1A cm^{-2} at 60 and 80°C** respectively corresponding to energy consumptions of **4,14 and 4,02 kWh Nm^{-3} (H_2)**.

III.2 Gas purity

The rate of hydrogen in oxygen measured increased during the test until the stop of the test (value higher than 2% of H_2 in O_2).

NB: there was a problem on the analyzer of the CEA bench on this test. These values are probably not perfect and are given in a comparative way between the beginning and the end of the test. Values measured for the MEA n°3 are probably closer to the reality.

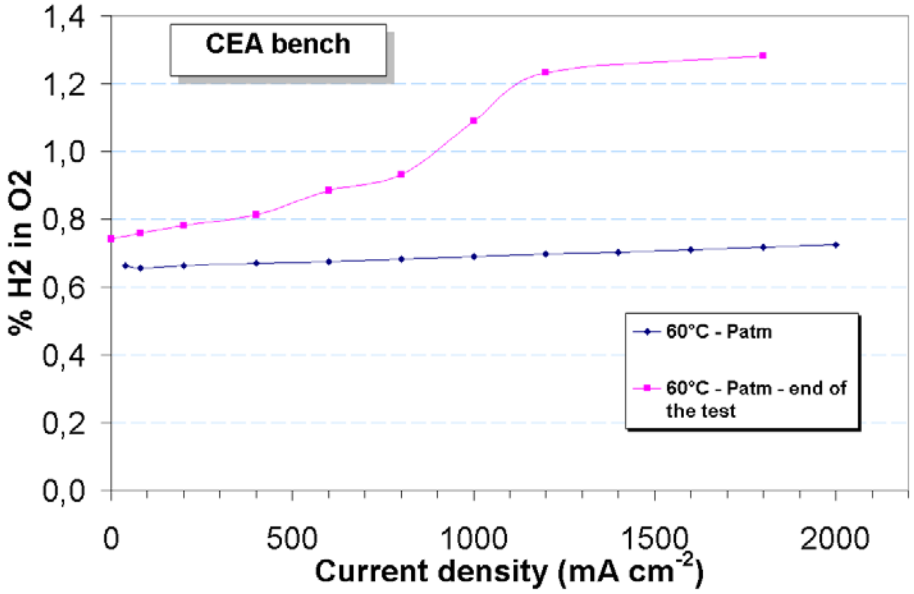

Figure 5: Evolution of the gas purity (oxygen) during the test

III.3 Lifetime

The evolution of the parameters (I, U, % H_2 in O_2) during time at 60 °C for the MEA n°2 are presented below.

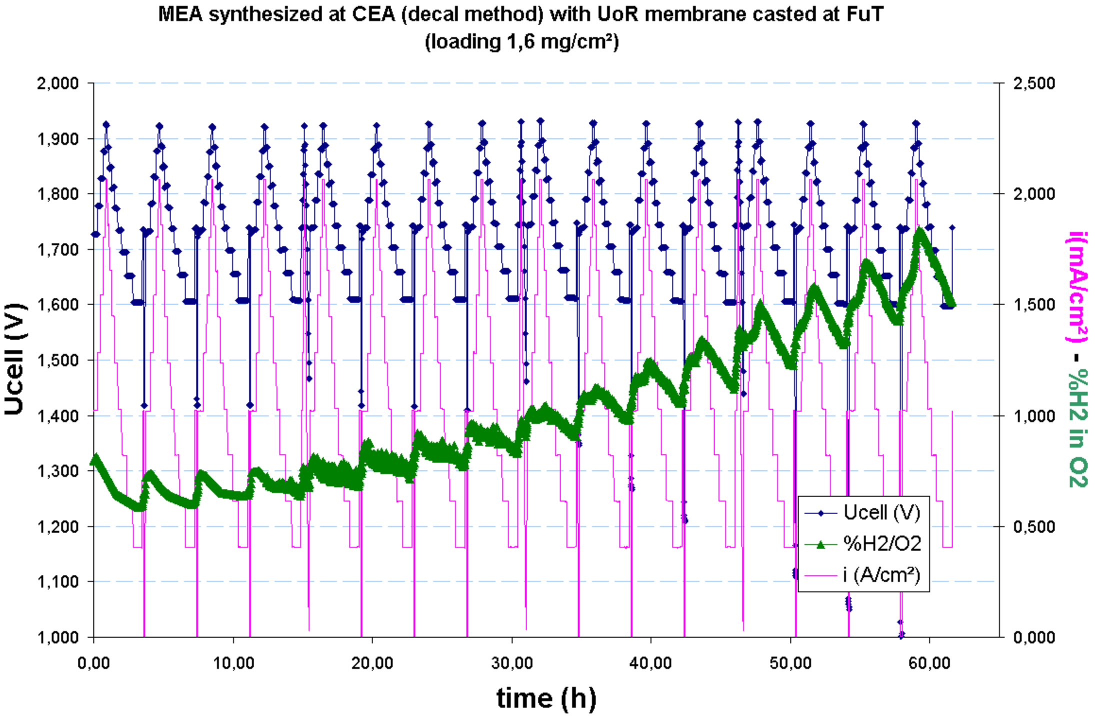

Figure 6: evolution of parameters (U, I, gas purity) vs. time for MEA n°2 at 60°C

The main observations are that:

- Electrical performances are good and stable
- Values of H_2 in O_2 are high and increase with time but <2%
- The test was stopped after 60h

III.4 Conclusions

Principal conclusions for this MEA are:

- Very interesting performances were obtained
- The performances stability is interesting for 60 h
- Acceptable purity of the gas measured: to be confirmed with a new MEA (after analyzers calibration)
- No information in electrochemical impedance spectroscopy: test stopped before.
- The MEA was degraded with big holes and delamination of the electrocatalytic layers. This was mainly observed on the contour of the active surface area corresponding to the effects of the edges of the sintered disc or GDL.

IV. MEA n°3

IV.1 Conditioning

The evolution of the polarization curves during the conditioning of the MEA at 60°C is given below. Here, the conditioning was long (week end) and give information about the stability of the MEA.

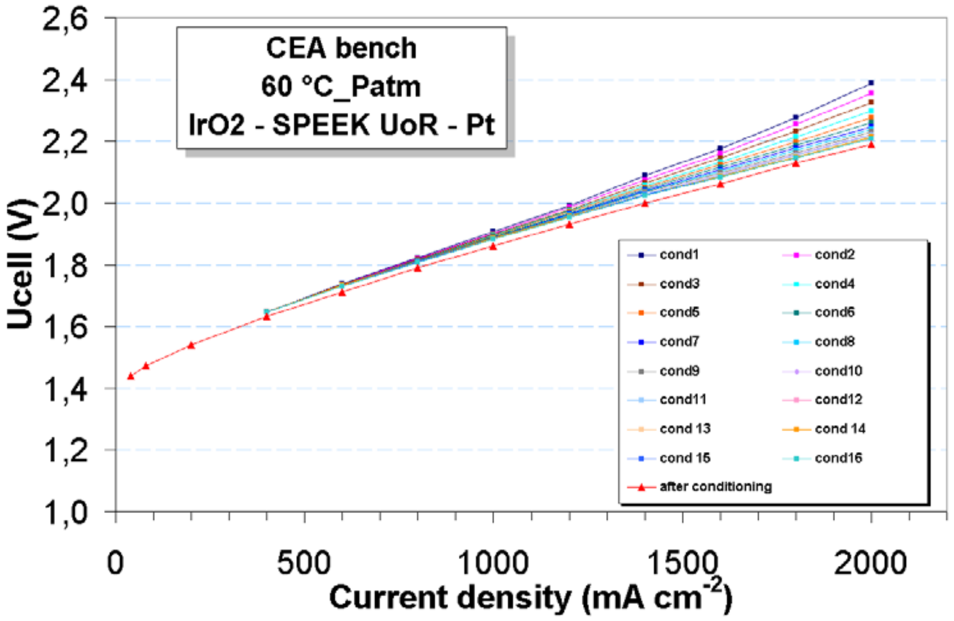

Figure 7: Evolution of performances during the conditioning for the MEA n°3

Performances are better with the time. This could be explained by a progressive hydration of the membrane and of electrocatalytic layers. This was less observed for the MEA n°2 which had a lower loading of dioxide iridium on the anodic side (explanation?).

IV.2 Performances

The best electrical performance obtained at 60°C and atmospheric pressure after conditioning is shown after:

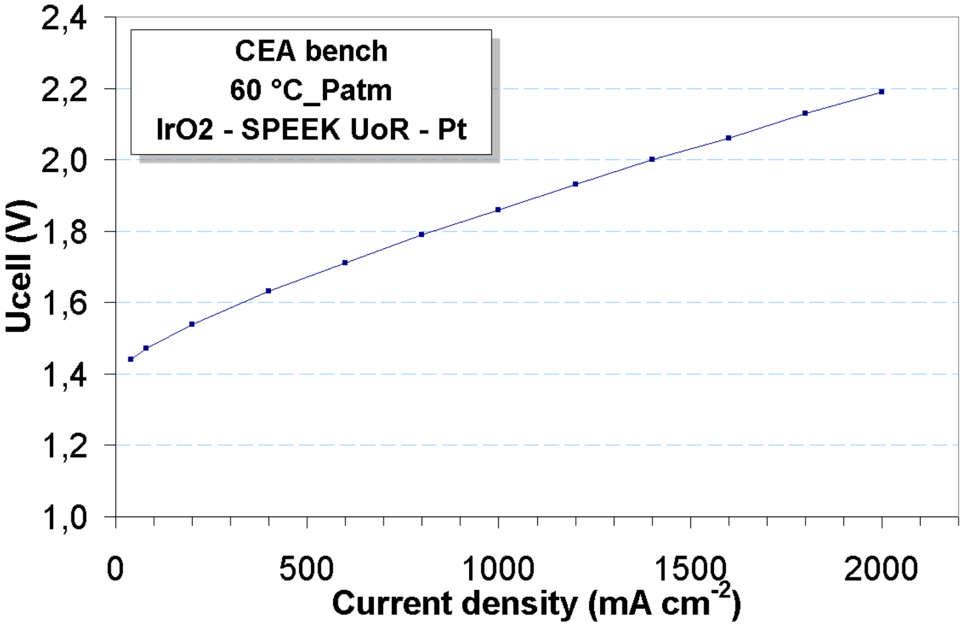

Figure 8: Polarization curve at 60°C - Patm obtained for the MEA n°3

The electrical performance obtained for this water electrolysis monocell test is interesting with **1,86 V at 1A cm^{-2} at 60 °C** corresponding to an energy consumption of **4,44 kWh Nm^{-3} (H_2)**.

At 80 °C, the membrane was probably perforated because the gas crossover brutally increased and the test was stopped.

IV.3 Gas purity

The permeation of hydrogen in oxygen was decreasing during the conditioning time. The rate was around **0,6 % of H_2 in O_2** at 1 A cm^{-2} and 60°C which is higher than the value measured at 25°C in the permeation test (**0.055 %**). The effect of the temperature and of the clamping of the MEA in a cell test may be one reason of such difference.

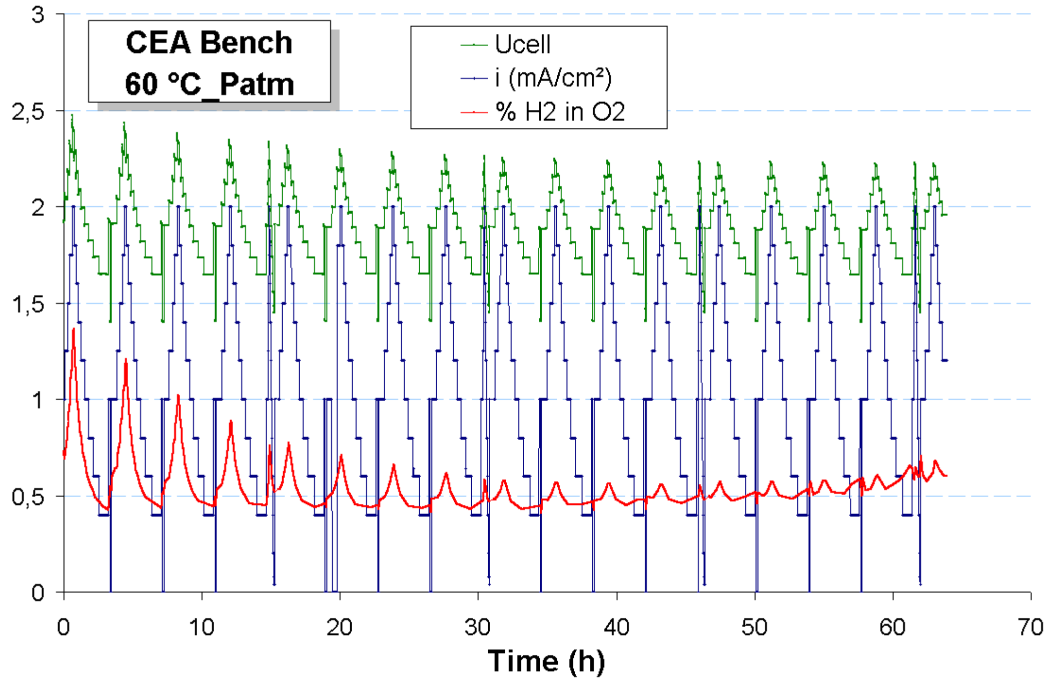

Figure 9: Evolution of parameters vs. time at 60°C

The % of H_2 in O_2 increased dramatically when the cell was raised at 80°C. The test was stopped after around 60 h as observed with the first MEA. The MEA was degraded with big holes and delamination of the electrocatalytic layers

IV.4 Electrochemical Impedance Spectroscopy

Electronical impedance spectroscopy measurement was performed at 60°C for this MEA.

The frequency range typically used for impedance spectroscopy characterization of PEM electrolysis MEAs is generally comprised between a few tens of kHz and several hundred MHz.

Depending on the equipment used, it is possible apply a current or a voltage signal. The amplitudes of the signals can be highly variable, but mainly for measurements of impedance spectroscopy to observe the following conditions:

- Linear response over a solicitation (user refines U = f (j))
- Stationary (not changing the system over time)

It is essential to define accurately the frequency range, the type of solicitation electrical (current or voltage) and the amplitude of the signal. Here the frequency range was between 10 kHz and 200 mHz.

Nyquist diagram plotted at different current densities at 60°C are presented below:

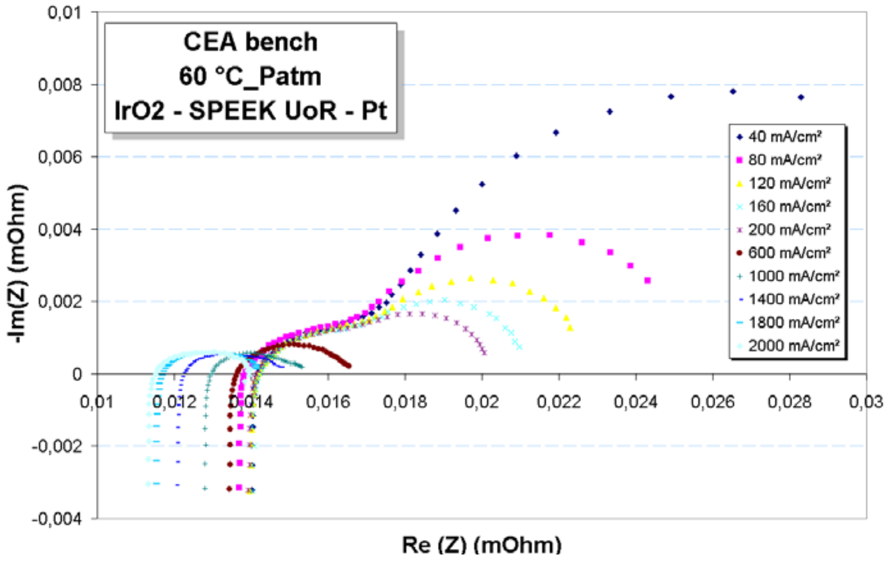

Figure 10: Nyquist diagram for different current densities at 60°C-Patm

Polarization resistances and ohmic resistance could be plotted as function of the current density as presented below.

The value of the ohmic resistance is around **350 mΩ cm²** which is a little higher than values generally observed for N115 in same conditions (**200-250 mΩ cm²**). However, it can be observed a little decrease of this resistance when the current density increases which could be associated to a local increase of the temperature (better conductivity of the protons).

The conductivity could be evaluated. Indeed, the ohmic resistance is around $R_\Omega \approx R_{\Omega\text{membrane}}$ and:

$$\sigma = \frac{L}{R_\Omega S}$$

σ: conductivity (S cm^{-1})

R_Ω: ohmic resistance (Ω)

L: thickness (cm)

S: surface area (cm²)

The conductivity calculated for the SPEEK membrane is **0.11 x 10^{-1} S cm^{-1}**. This value is lower than the value of the Nafion[1] (around 10^{-1} S cm^{-1}).

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[1] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster., **Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology.,** *Chem. Rev, 104, 4637-4678,* (2004).

NB: there may be an important contribution of the ohmic resistance of the electroactive layer as the loading is important at the anode (thick layer). Besides, as the binder of the ink was Nafion, the resistance of interfaces membrane/electrode is probably not negligible.

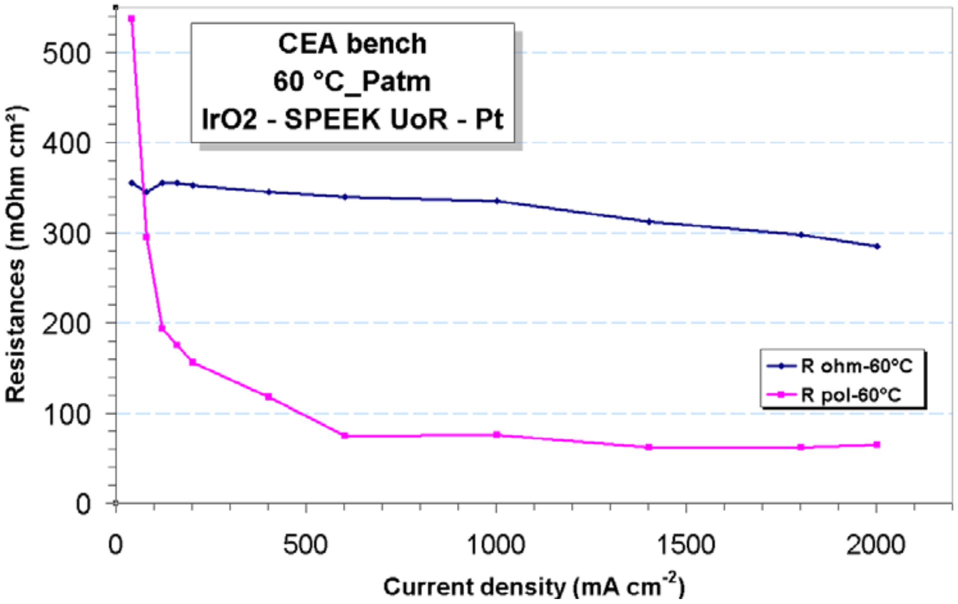

Figure 11: Evolution of the resistances in function of the current density

The polarization resistance decreases with the increase of current density and stabilizes at high current densities as generally observed (part the polarization curve guided by ohmic contribution).

IV.5 Conclusions

Principal conclusions for this MEA are:

- Interesting performances were obtained but lower than for the MEA n°2
- The performances stability is interesting for 60 h
- Degradation before results at 80°C
- Acceptable purity of the gas measured
- The conductivity of the protons of the MEA is not sufficient: probably because the interface ink/membrane should be improved
- The MEA was degraded with big holes and delamination of the electrocatalytic layers. This was mainly observed on the contour of the active surface area corresponding to the effects of the edges of the sintered disc or GDL.

V. Conclusions and next steps

MEA tested with the SPEEK membrane synthesised by the university of Reading showed very interesting electrical performances.

Besides, the gas permeation is acceptable (comparable to the Nafion) which is interesting for such a thin membrane (40 µm).

The membrane presented a good stability during around 60 h but tests were stopped brutally with important mechanical degradation.

Other tests will be performed with MEA composed of the Ir/ATO on the anodic side (innovative catalyst of the NEXPEL project).

The membrane should be thicker than 40 µm or reinforced in order to enhance the mechanical resistance and the durability of the tests.

Appendix 2: SINTEF - Testing of UoR sPEEK membranes in membrane electrode assemblies at SINTEF

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Memo

Testing of UoR sPEEK membranes in membrane electrode assemblies at SINTEF

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1 Introduction

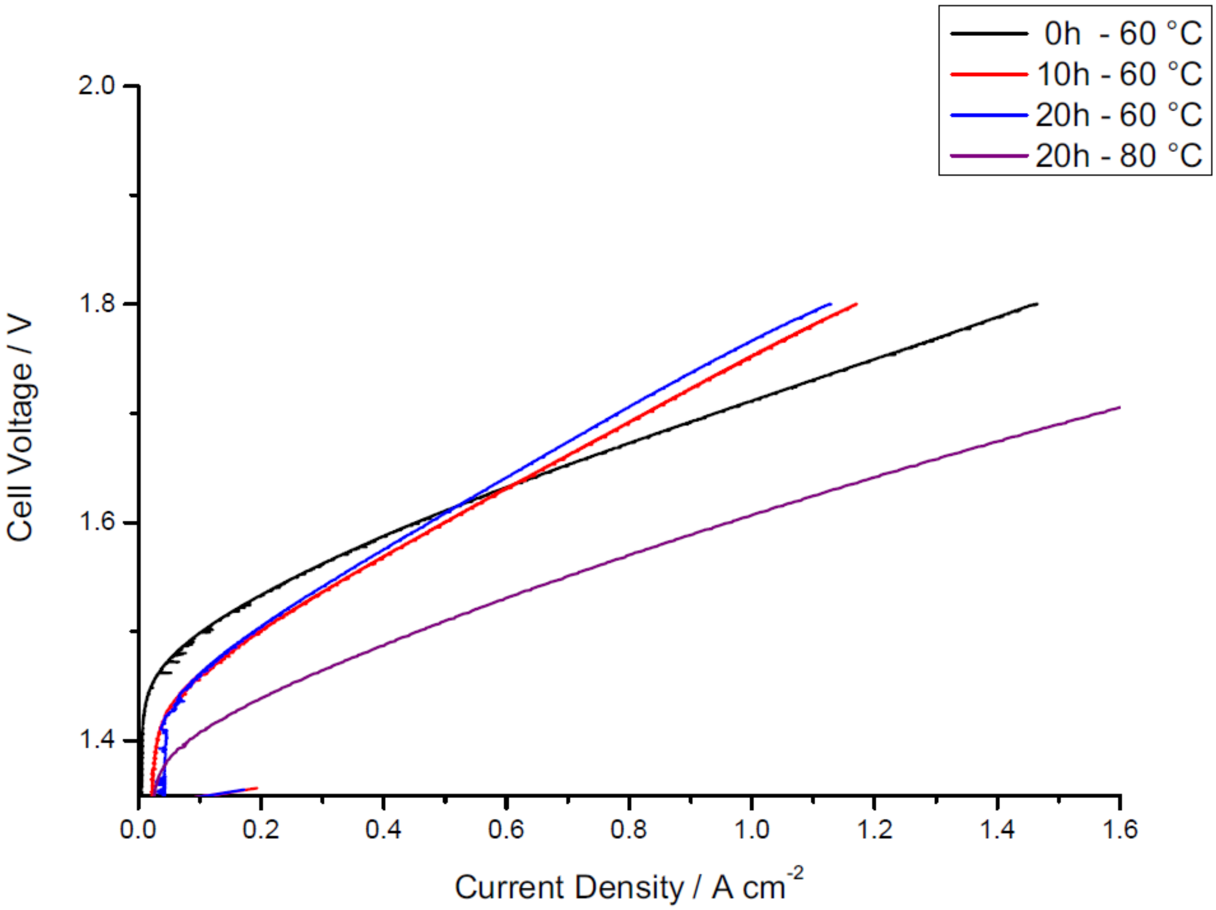
An attempt of making a MEA of a hydrocarbon based membrane developed at University of Reading and casted at Fumatech was made at SINTEF. The goal was to coat the membrane with catalyst and test the performance and durability in a PEM electrolyser.

2 MEA preparation

Ir/ATO catalyst particles were added to a solution consisting of a mixture of isopropanol and water (50/50 wt%) in an amount resulting in a total concentration of solids of 2wt%. Nafion ionomer solution was then in sufficient amount to obtain 7.5wt% Nafion in the final catalyst layer.
The mixture was ultrasonicated for 30 minutes and stirred for another 30 minutes. The membrane was weighed out then mounted in a 25 cm2 frame and put on the hot-plate at 85°C. The ink was carefully sprayed on the membrane using air brush then it was left on the hot-plate for 10 minutes to dry. Then the membrane was then further dried in the oven at 100 °C for 15 minutes to make sure there is no water remaining in the catalyst layer to interfere weight measurement. The membrane with catalyst was

weighed out then subtracted from the membrane's weight to get the loading. A final loading of 1 mg Ir/cm^2 was obtained.
A standard E-TEK gas diffusion electrode with a Pt loading of 0.5 mg/cm^2 was used as a cathode and attached to the membrane by hot-pressing at 130 °C with 18 kg/cm^2 for 1 minute.
The prepared MEA was immersed in DI water for one hour before being mounted in a Baltic Fuel cell test cell.

The cell was heated to 60 °C and a polarisation curve was recorded. The cell was then operated at 1.7V and additional polarisation curves were recorded at 10h and 20h of operation. The series of polarisation curves at 60 °C show that there is an initial break in period during the first 10h where the electrodes are activated. However, the cell resistance is also increasing during the first 10h which could be related to a reduction of the proton conductivity of the membrane. To elucidate this, additional experiments are needed.
The cell was then heated to 80 °C and a polarisation curve was recorded. The cell was then operated at a constant voltage of 1.7V for 4h before a critical failure of the MEA forced an emergency shut down of the test. A visual inspection of the MEA revealed a large crack in the membrane at the edge of the catalyst coated area.



The results show a relatively good performance of the MEA with comparable or lower resistances than state of the art MEAs for PEM electrolysers. This reduced resistance is most probably due to the thinner membrane used in this MEA than in standard PFSA-based MEAs. This test shows that it is, without any major changes in the manufacturing process, possible to make catalyst coated membranes with the sPEEK membrane made by UoR/Fumatech.

The thin membrane in the MEA is also most probably the cause of the mechanical failure of the MEA and the emergency shut down after about 30h of operation. This could be remedied by reinforcing the whole membrane or adding an edge reinforcement film.

Appendix 3: FuMA-Tech - Fabrication of CCM based on membrane from UoR

Fabrication of CCM based on membrane from UoR

1. Preparation of catalytic ink and coating experiments

Two kinds of inks for both cathode and anode have been prepared: one kind of ink contained as polymer (and binder) the SPEEK material, the other one was standardized material with PFSA.
Both inks were prepared for aim of direct coating on the membrane, which is state-of-the-art technology of CCM employed at Fumatech.

The SPEEK material used as solvent DMAc (di-methyl aced-amid) and it had to be diluted to relatively low concentration of solid content due to high viscosity of used materials in order to achieve some reasonable process-ability of this kind of ink on the ink-jet air-assisted coating device.
However, it turned out during the coating process that the coated layer delaminates so only very thin coated layer has been achieved.
When a screen-print device has been used, it has been concluded that a separation of phases happens on the sieve and again, almost no catalyst has been transferred to the surface of the membrane.
For above mentioned troublesome operation, SPEEK polymer has been dismissed from further use in these experiments.

Better result has been achieved with PFSA as ionomer. The adhesion of the catalyst toward membrane was not particularly high, but some reasonable coating level (0,35 mg/cm2 of Pt and 2 mg/cm2 of Ir) has been achieved. Here one has to note that because of excessive swelling of the membrane, very thick catalytic inks had to be fabricated that were on the top limit of process-ability of the coating device. Standard Pt-ink has about 6-8% of solid content while the used one contained 10,5% of solids. As for Ir, the content of solid phase was set to 25%, which would cause possibly some diffusion effect of the anodic layer during the operation, but the coating became realistic and the membrane did not swell too much so a well defined shape of CCM was prepared.

2. Mounting of the CCM into cell

There were prepared in total three CCMs of the active area 63,6 cm^2 (dia 90 mm circular), which is standard characterisation cell of Fumatech.
Because of the thin membrane, it was feared that the membrane might not survive the assembly procedure and above all the tightening toque. For this reason, a lamination of membrane with some protective foil has been adopted. First, the membrane was laminated by adhesive foil and set into testing cell. As a sealing, an O-ring was used; on the other side, a machined space fits the thickness of the O-ring.
However, the membrane broke immediately after assembling so no data could have been recorded. This breakage has been demonstrated and confirmed still during the experiment by very low resistance of the cell (=shortcut occurred). It was noted that membrane also did not have enough room to swell and expend and for this reason an alternative way has been sought for.
It was supposed that the membrane should be handled more carefully to give it space also for possible swelling, which might equalise the surface irregularities of dried membrane. So a two 175 µm layers have been put as free protection. However, also in this case the membrane did not survive and broke during assembling.
The third piece was built-in as it was, i.e. without any protection foil, but it failed again.

3. Conclusion

It was concluded that the SPEEK membrane is at the time of fabrication less preferred candidate for CCM preparation for several reasons, above all for the poor behaviour during setting-in. However, a more sophisticated lamination might make it possible and the CCM could be worth of testing. Another alternative way would be testing it in some experimental cell that is less demanding on the tightening. In addition, some transferred method such as decal would also possibly suit more to the CCM fabrication rather than direct spraying.