

Long-life PEM-FCH & CHP systems at temperatures $\geq 100^{\circ}\text{C}$ (G.A. 245339)



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Application Area: SP1-JTI-FCH.3: Stationary Power Generation & CHP

Project type: Research and Technological Development

Topic: SP1-JTI-FCH.3.3 Degradation and lifetime fundamentals

Start date: 01-01-2010 End date: 31-12-2012

Duration: 36 months

Project total costs: € 2.927.174

Project funding: € 1.360.277

Partner number	Partner name	Country
1 (coordinator)	CNR-ITM (CNR)	Italy
2	The University of Roma "Tor Vergata" (URoma2)	Italy
3	Aix-Marseille Université (UProvence)	France
4	The University of Saarbruecken (USaar)	Germany
5	Edison	Italy
6	Fumatech	Germany
7	MATGAS 2000 A.I.E. (MatGas)	Spain
8	Cracow University of Technology (CUT)	Poland

Project Structure

URoma2

CNR
Fumatech
UProvence
Usaar

WP1 – Long-life
membranes for
PEMFCH

Usaar

WP2 – New
concept of MEA
with improved
durability

CNR

MatGas

WP3 – Life-time tests
and prediction
techniques,
establishment of
accelerated test
technique

Usaar
Edison
CNR
Fumatech

CUT

WP4 – Dissemination
and exploitation of
results

URoma2
Fumatech
UProvence
Usaar

Edison

MatGas

CNR

Project goals, targets, and milestones


The **main objective** of the present project is to give a clear demonstration that **long-life SPG&CHP systems based on PEMFCHs operating at temperatures $\geq 100^{\circ}\text{C}$ can now be developed** on the basis of recent knowledge on the degradation mechanisms of membranes disclosed by some participants in this project.

Milestones

Milestone no.	Milestone name	Delivery date from Annex I
M1	Kick off meeting	achieved
M2	PFSA membrane stability ex-situ test	achieved
M3	SAP membrane stability ex-situ test	achieved
M4	Single PEMFCH design and building	achieved
M5	Modular multi-cell system design and building	achieved
M6	Degradation and lifetime test	achieved
M7	Innovative MEA operating above 100°C	achieved
M8	Cost of use and discard MEA	achieved
M9	Publications, patents, conferences	During the project activity

Specifications foreseen in LoLiPEM project

PEM parameters	PFSA	SAPs
	End of project	End of project
operating temperature of membrane (maximum)	120°C	140°C
operating temperature in fuel cell (maximum)	120°C	140°C
membrane conductivity @ 90%RH	> 0.1 S/cm	> 0.07 S/cm
liquid water uptake @ 100°C	40%	< 50%
mechanical integrity @ RH cycling and condensing conditions	Yes	Yes
MEA performance @ 0.65 V	0.7 A/cm ²	0.7 A/cm ²



To improve the durability and stability of the MEA at a temperature higher than 100°C, the following new strategies have been applied :

For membranes:

- Thermal annealing & Chemical cross-linking

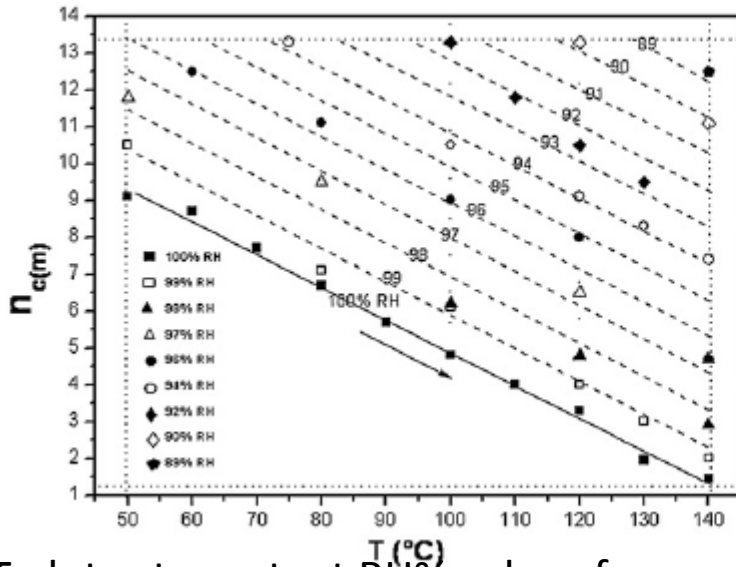
- For the catalyst

- novel electrodeposition techniques from precursor layers, which enables to deposit electrocatalysts directly onto gas diffusion layers (GDL) and thus transforms them directly into gas diffusion

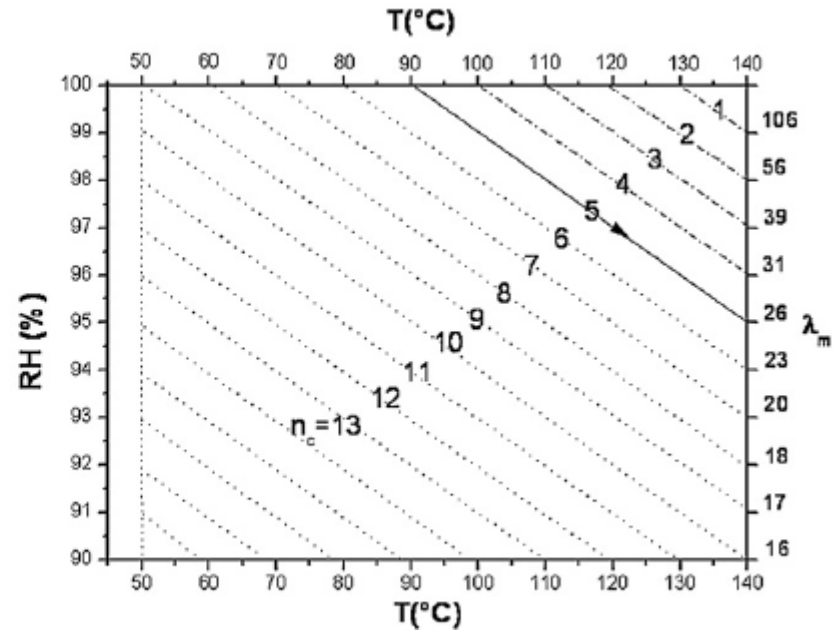
- For MEAs

- Novel procedure for MEA preparation including pre-treatment of the membrane, slow heating and cooling during the hot pressing

PFSA MEMBRANE

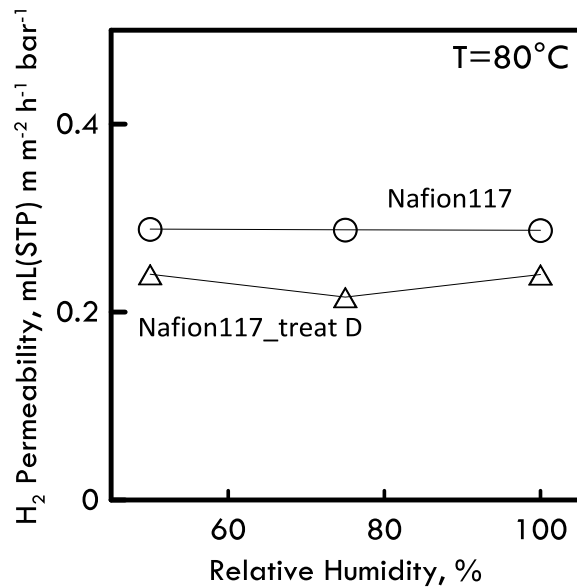


n_c - T plots at constant RH% values for Nafion 117 membrane (annealed at 120°C for 15 h)

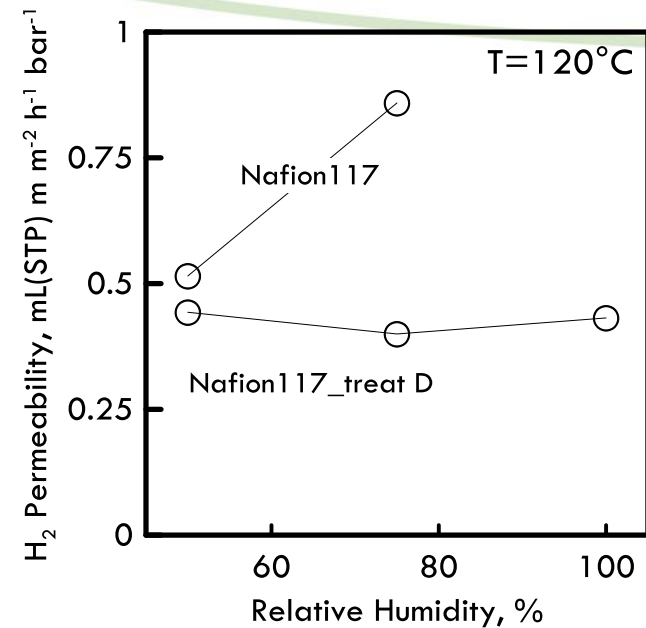


Conversion of the left plots in T-RH% plots for constant n_c values. The zone with n_c values < 6 represents an instability zone for temperatures $> 80^\circ\text{C}$ when $\text{RH}\% = 100$.

PFSA MEMBRANE

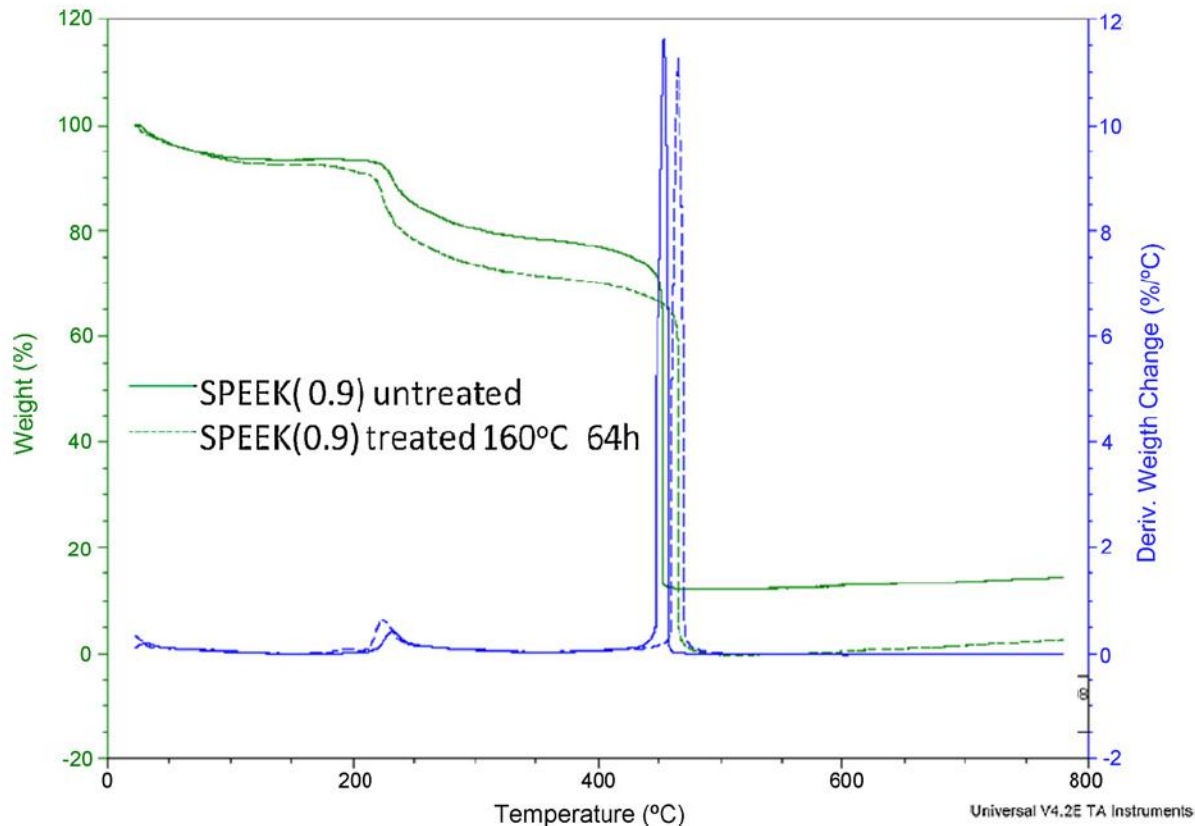


Globally, the Nafion 117 thermally annealed showed a lower permeability than Nafion at all the operating conditions investigated.



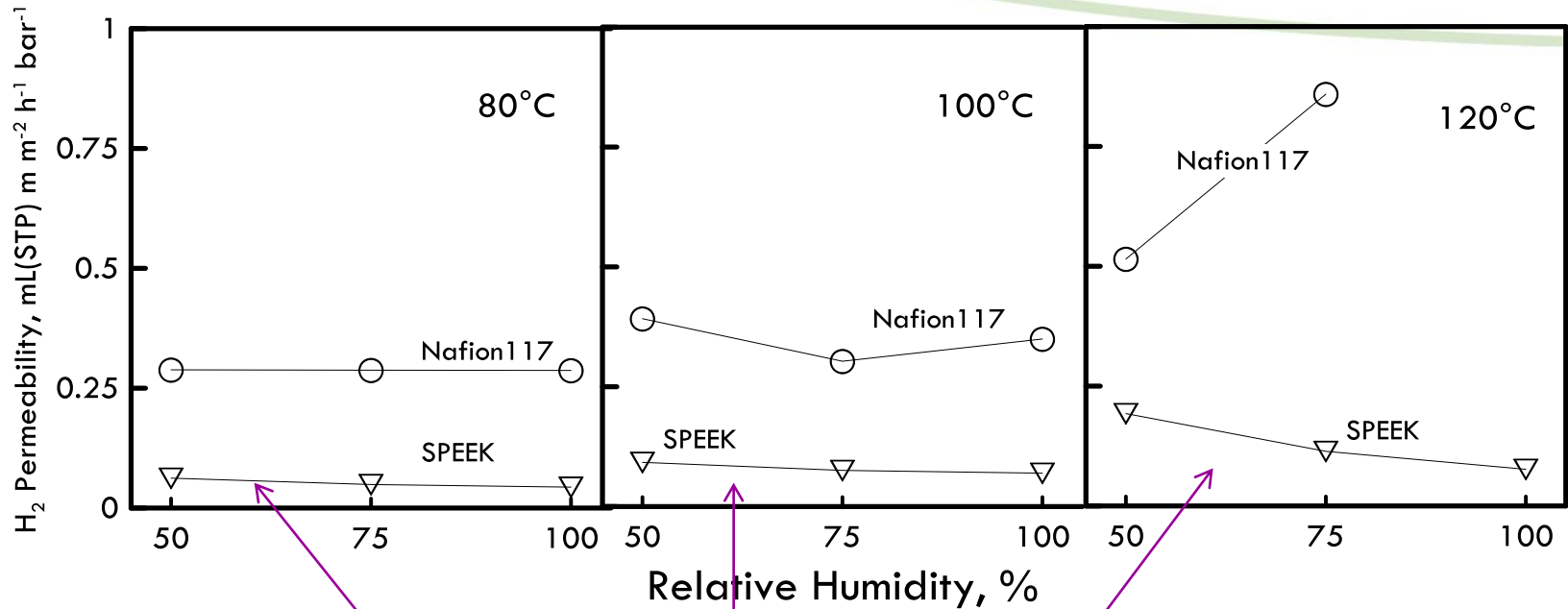
At 120°C, the Nafion thermally annealed continued to exhibit a stable trend contrarily to what happened for the Nafion that showed an unstable behavior yet at RH equal to 75% and was broken at RH of 100% .

SAP MEMBRANE



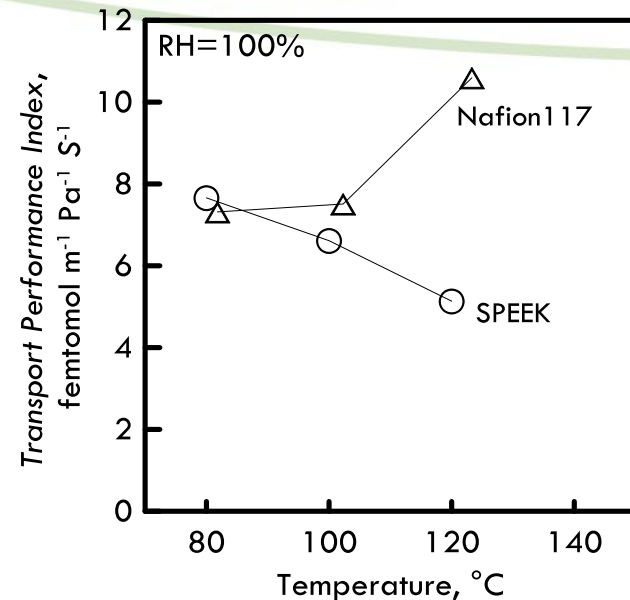
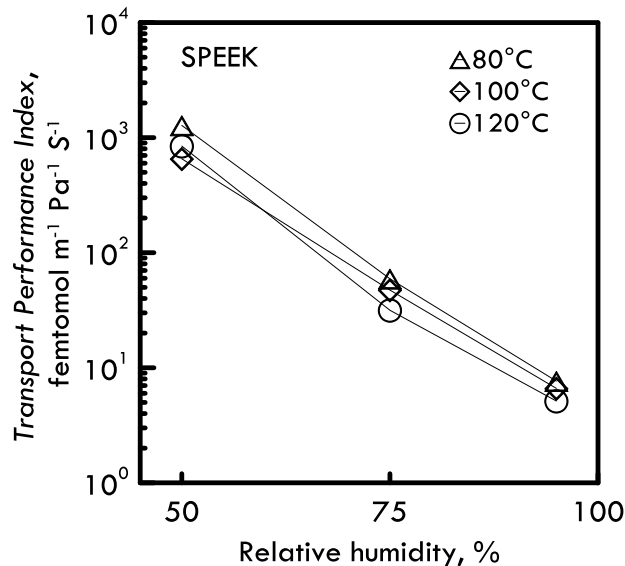
Comparison of thermogravimetric curves for untreated (solid line) and annealed (dashed line) SPEEK with initial DS = 0.9. The reduction of second mass loss due to sulfonic acid groups for annealed SPEEK can be related to the degree of cross-linking between macromolecular chains.

SAP MEMBRANE



SPEEK shows a lower permeability than Nafion 117 at all the operating conditions investigated.

$$\text{Transport Performance Index (TPI)} = \frac{2 \cdot H_2 \text{ Permeability}}{\text{Proton conductivity}}, \quad \text{mol s}^{-1} \text{ Pa}^{-1} \text{ S}^{-1}$$



The comparison of TPIs between SPEEK and native Nafion 117 highlighted the advantage offered by the SPEEK membrane.

- The TPI of SPEEK got the higher value at 80°C, afterwards it started to decrease as the temperature increased.
- The Nafion 117 membrane, starting at 80°C from the same value of SPEEK, exhibited an increasing trend in the whole temperature range.
- TPI of the SPEEK, was always lower than the Nafion 117 one, for temperature higher than 80°C

MEMBRANE

	Permeability (barrer) @ 100% RH		
	H ₂	O ₂	N ₂
Nafion 117	118	64.3	29
Nafion 117 thermally annealed	87.6	38.9	22.5
SPEEK – Thermally annealed	15.9	3.5	4.3
SPEEK-WC(0.86) no CL	20.2	7.44	3.85
SPEEK-WC(0.86) CL with DAMP for 1.5 h	16	5.6	Under detection limit

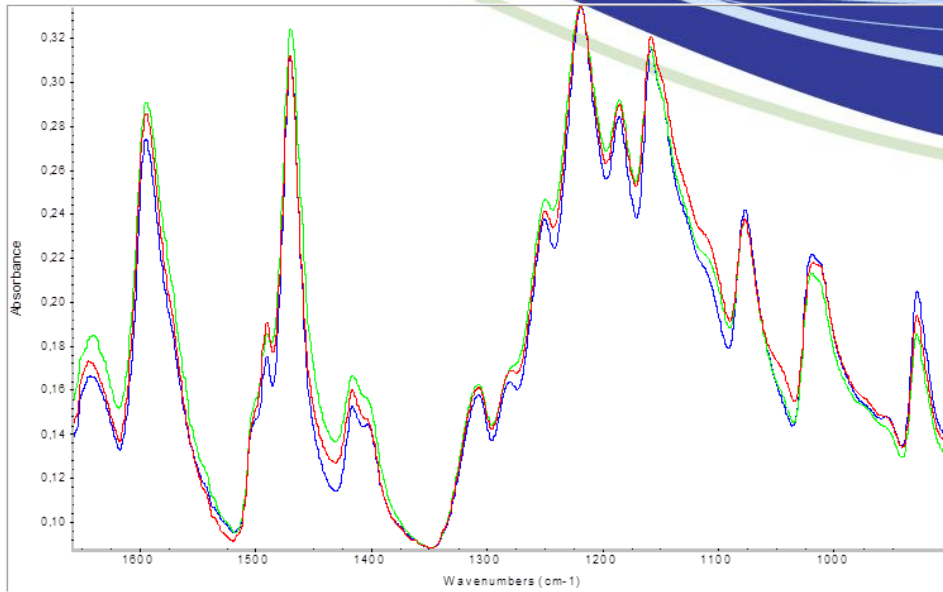
MOPEM

The MoPEM-CHP system has been designed as an innovative stack for the easy replacement of PEMFCHs and the facilitated use and discard of MEA.

The system is designed to allow adiabatic operations maximizing the recovery of heat produced.

The elements of the MOPEM have been properly designed for the innovative configurations of the system.

Post Mortem analysis ... some results



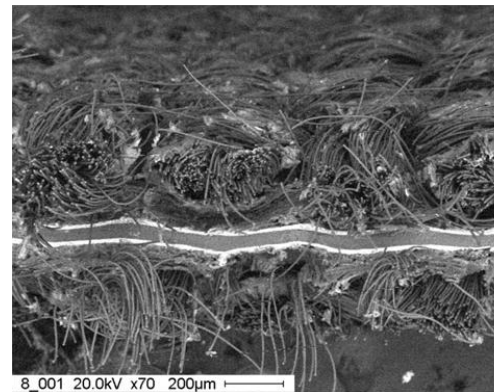
The FT-IR/ATR spectra of **SPEEK BM50/MEA active area** (green line), **SPEEK BM50/MEA no-active area** (red line) and **SPEEK LP29** (blue line, bare membrane) do not show any significantly difference

SEM images:

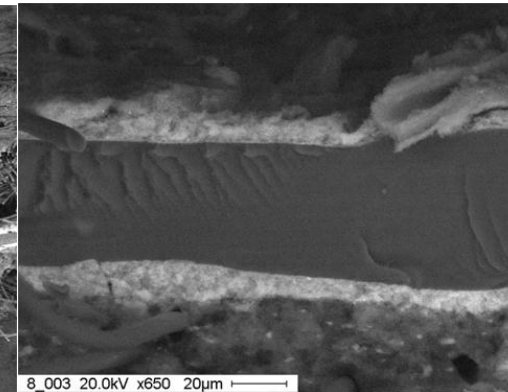
membrane SPEEK BM50

anode and cathode: ELAT E-TEK+SPEEK

SEM/BSE images do not show Pt particle penetration inside the membrane

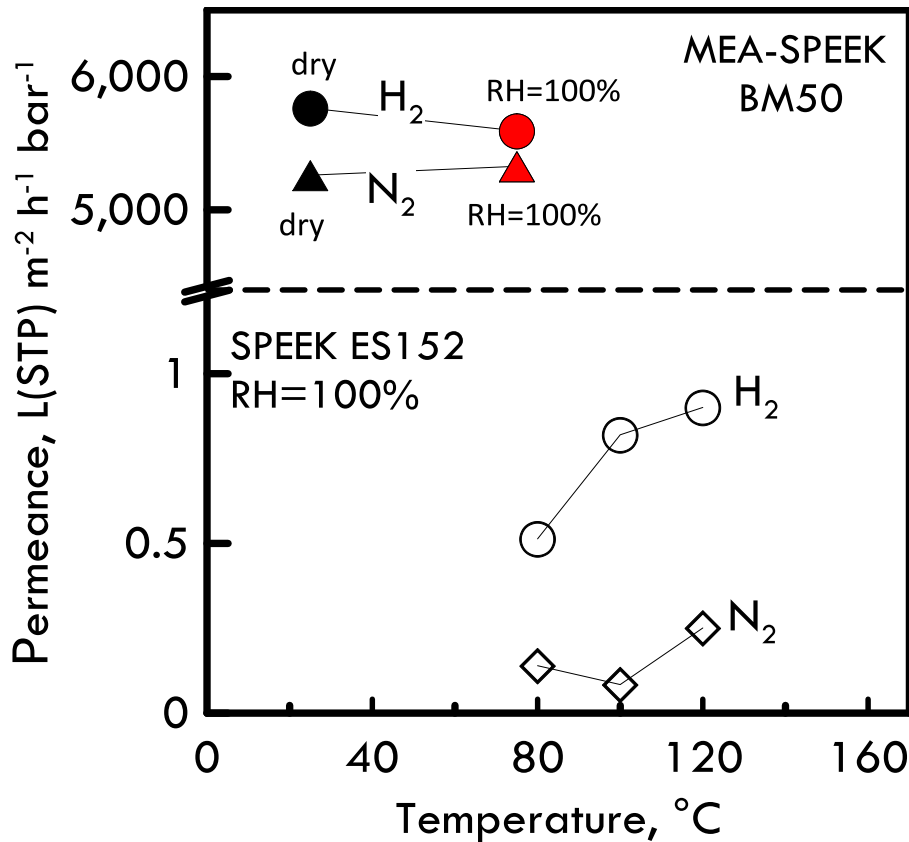


Magnification x70
SEM – BSE detector



Magnification x650
SEM – BSE detector

Post Mortem ... some results

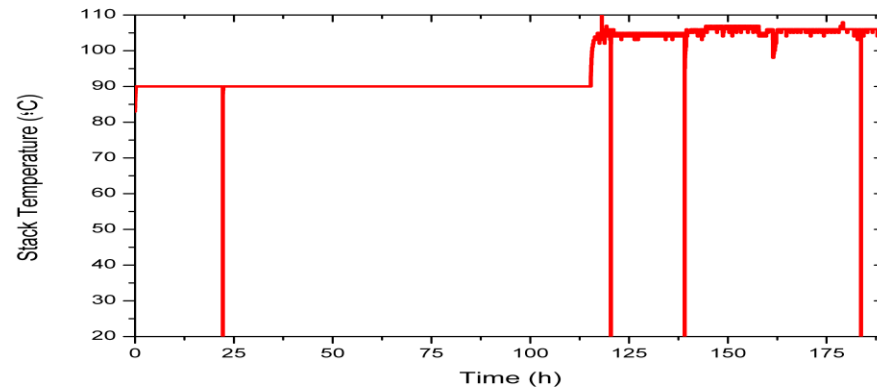
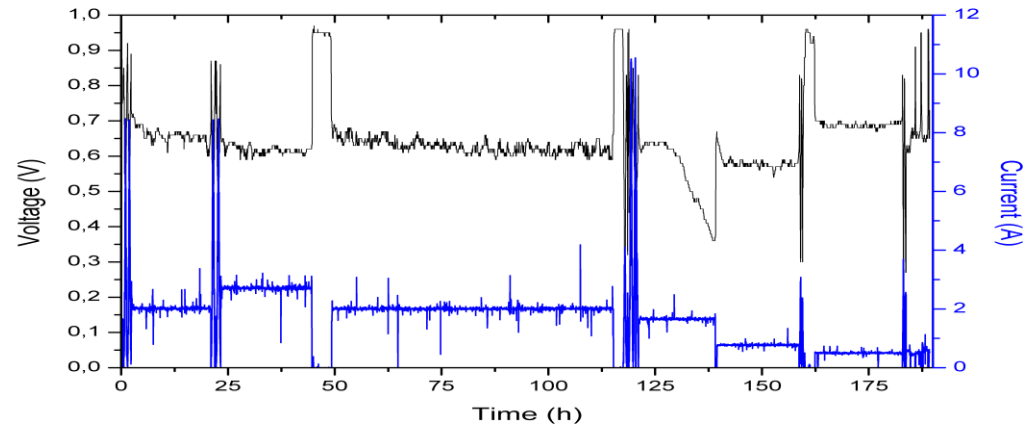


The permeances exhibited by the MEA is more than **3 order** higher than the ones measured on a membrane similar to the one present in the MEA.

This behaviour confirms the presence of macrodefects in the membrane inside the MEA.

Long term testing

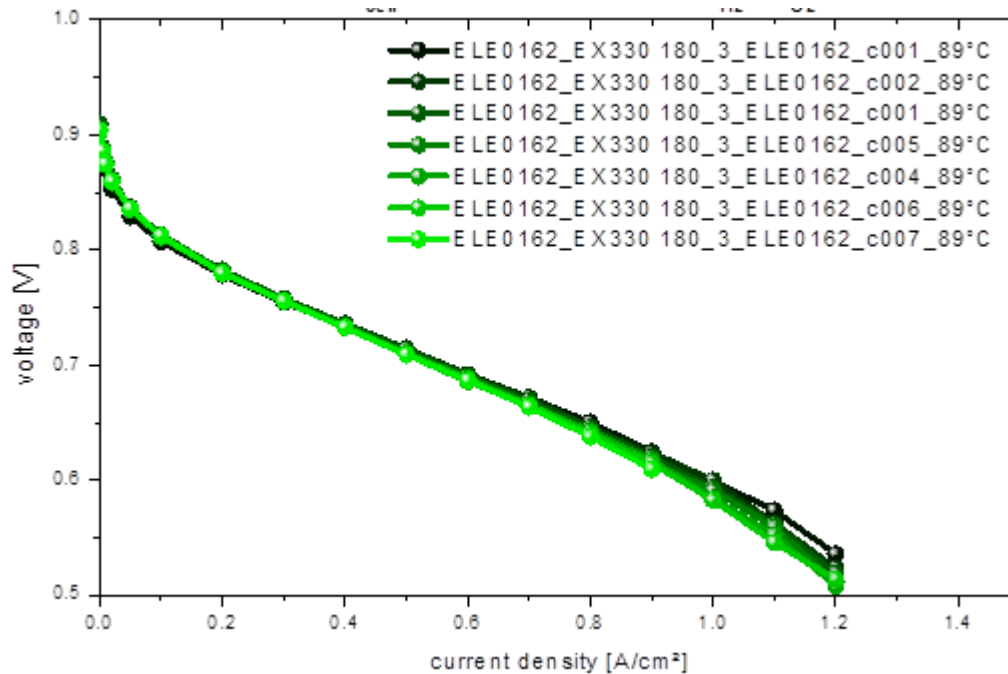
MEA	Origin	Activation	Max T_Stack	Duration
ELE0162/NR212/ELE0070 Nafion thermal annealed	USAAR/ URoma2	24h at room T	105°C	189.23h



Successful tests
carried out at 105°C

Electrical Measurement

- Polarization Results



- 0.8 A cm⁻² @ 650 mV
- 0.4-0.5 mΩ

Alignment with MAIP

MAIP Section 3.4.3 Stationary Power Generation & Combined Heat & Power

The overall objective is to improve the technology for fuel cell stack and balance of plant components to the level required by the stationary power generation and CHP markets by bridging the gap between laboratory prototypes and pre-commercial systems.

MOPEM

Long-term and breakthrough orientated research will concentrate on degradation and lifetime fundamentals related to materials and typical operation environments for relevant power ranges.

New membranes and electrodes

The aim will be to deliver new or improved materials as well as reliable control and diagnostics tools both at component and system levels.

Strategy for Post mortem analysis

Research and technological development will be directed towards developing components and sub-systems as well as novel architectures for cell and stacks leading to step change improvements over existing technology in terms of performance, endurance, robustness, durability and cost for all technologies.

New membranes and electrodes

MOPEM

Alignment with AIP

SP1-JTI-FCH.3: Stationary Power Generation & CHP

Development of control and diagnostics tools for operational performance including degradation and lifetime prediction (PEMFC, MCFC, SOFC technologies).

Durability tests
Accelerated tests
Strategy for Post mortem analysis

Development activities on component and system in order to meet application-relevant functional and performance criteria (PEMFC, MCFC, SOFC technologies).

New membranes and electrodes

MOPEM

Research on factors impacting the degradation and lifetime of stacks (SOFC, PEMFC, MCFC technologies); exploration of synergies with back up and UPS units.

Strategy for Post mortem analysis

Some of the major results

PEM parameters	PFSA	SAPs
operating temperature of membrane (maximum)	140°C	140°C
operating temperature in fuel cell (maximum)	105 °C	115°C
membrane conductivity @ , 90%RH	0.03 S/cm	0.091 S/cm SPEEK (180°C – 10 h)
liquid water uptake @ 100°C	<u>32%</u>	48% SPEEK (thermally treated at 180°C–20h) 25% (SPEEK-WC) 18% (SPEEK, Fumion E-490)
mech. integrity @ RH cycling and condensing conditions	Yes	Yes
MEA performance @ 0.65 V	0.8 S/cm still after 180 h	0.8 S/cm

Dissemination & public Awareness

Portals Search:

LoLiPEM

LoLiPEM is a research project devoted to the development of new membranes, electrodes and a CH₄ module for stationary power generation. Subcombined heat and power (CH₄ & CHP) systems, based on Polymer Electrolyte Membrane Fuel Cell (PEMFC) (PEMFC).

A PEMFC operating in the temperature range of 100-130 °C is highly desirable and could be decisive for the development of SPG & CHP systems based on PEMFCs.

LoLiPEM aims to operate in the temperature range above 100 °C exceeding the state-of-the-art (70-80°C) which represents the main drawback for the PEMFC development.

Operating temperatures above 100°C could have several advantages including easier warm water distribution in buildings, reduced anode poisoning due to carbon monoxide impurities in the fuel, improved fuel oxidation kinetics, etc.

The main objective of the LoLiPEM project is to give a clear demonstration that long-life SPG & CHP systems based on PEMFCs operating above 100 °C can now be developed on the basis of recent knowledge on the degradation mechanisms of ionomeric membranes and on innovative synthetic approaches recently disclosed by some participants of this project.

Some key points in the research activities are:

1. Development of long-life (longer 40000 hours) perfluoro sulfonic acid membranes and sulfonated aromatic polymer membranes operating at a current density of at least 4000 A m⁻²
2. Development of long-life catalytic electrodes and Membrane Electrode Assemblies (MEA)
3. Development of a prototype of a modular CH₄ & CHP system including more PEMFCs built with the new long-life MEAs
4. The understanding of degradation mechanisms, by means of accelerated ageing tests and long-term single cell measurements, in order to predict the lifetime and give feedback to the developing of membranes and electrodes
5. Benchmarking of the performance of a single-cell and the modular prototype against the best literature results.

The operating temperature of interest for the LoLiPEM project is in the range of 100-130 °C for both new membranes, electrodes, MEAs and the whole modular system.

The project will benefit of the synergy arising from the know-how of leading research groups of universities and research institutes as well as from the technical knowledge and expertise of industries and utility companies involved in fuel cell development and testing.

The project is supported by the Fuel Cells and Hydrogen Joint Undertaking

The web site www.lolipem.eu is operative and the project brochure has been printed and is available as pdf file

Dissemination of project results through conference presentations, publication in high impact international journals

Training/education of various fellowship and post-doctoral researchers in materials science, processing of ionomers, characterisation of polymer and inorganic electrolytes

Technology Transfer / Collaborations

- Information letter on the LoLiPEM project was sent to 197 European stakeholders in the field of hydrogen fuel cells technologies such as European and national Technology Platforms, NEW-IG members & supporters, N.ERGHY, companies, institutions.
- The exploitation activities foresaw a comprehensive definition of market-oriented aspects of the developed technologies of Fuel Cells and are summarised in “the strategy of exploitation”. The strategy put attention on potential markets, business models and management of IPR issues emerging during implementation of the project.

Thank you for your attention

