# LoLiPEM - Long-life PEM-FCH &CHP systems at temperatures ≥100°C (FCH-JU - G.A. 245339)

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Partner number	Country	
1 (coordinator)	CNR – Institute on Membrane Technology	Italy
2	The University of Roma "Tor Vergata"	Italy
3	The University of Provence	France
4	The University of Saarbruecken	Germany
5	Edison S.p.A.	Italy
6	FuMA-Tech GmbH	Germany
7	MATGAS 2000 AIE	Spain
8	Cracow University of Technology	Poland

# 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°C can now be developed on the basis of recent knowledge on the degradation mechanisms of membranes disclosed by some participants in this project.

In order to conciliate the achievement of the main objective with the need of durability, low cost and an easy management, investigation of several subobjectives will be necessary concerning development of stable and less expensive membranes, development of more stable catalytic electrodes as well as physical-chemical characterizations of the obtained products.

# Sub-objectives ...

- Creating stable Perfluoro Sulfonic Acid (PFSA, e.g. Nafion) membranes operating with current density at least 0.7 A/cm<sup>2</sup>
- Long term durability for stationary FC operation in air at temperatures by at least 20°C higher than that of the state-of-theart
- Creating new stable non perfluorinated ionomers, such as sulfonated aromatic polymers (SAPs, e.g. SPEEK, SPEEK-WC, Fumion, etc), much less expensive than PFSA in order to reduce the cost of the co-generation systems
- Reducing the costs by optimizing the water management and the cell pressure using new equations recently developed

# ... Sub-objectives

- Creating new catalytic electrodes more stable at the operating temperatures
- Reducing the cost of the high temperature FCH by facilitating the replacement ("use and discard") of MEAs
- Establishment of accelerated test techniques and lifetime prediction methods
- Benchmarking the single-cell performances at temperatures ≥ 100°C
- Prototype development of a Modular multi-PEMFCHs system for Combined Heat and Power
- Exploiting the results in terms of patents for the industrial partners, publications in high impact international journals and top international conferences, reaching out to the public and increasing the awareness of this technology

# 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
Durability @120°C	> 40.000 h within 10 years with start-stop	> 40.000 h within 10 years with start-stop
MEA performance @ 0.65 V	0.7 A/cm <sup>2</sup>	0.7 A/cm <sup>2</sup>

# Interdependencies among the





# **Project structure**

### WP1 – Long-life membranes for PEMFCH

- □ Preparation of stabilized Perfluoro sulfonic acid (PFSA) membranes
- □ Cross-linked sulfonated aromatic polymers (SAP) membranes
- □ Ex-situ characterization of stabilized membranes.
- Permeation measurements for the evaluation of mass transport properties of the membranes

### WP2 – New concept of MEA with improved durability

- $\Box$  Catalytic electrodes for temperature > 100°C
- Membrane-electrode assembly (MEA)
- Design of use and discard MEAs: Design of a MoPEM system for facilitating the installation and replacement of a single PEMFCH.

# **Project structure**

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

- Durability studies of PEM-FCH & CHP system at temperature 100°C. Accelerated aging durability studies
- Long-term durability tests
- ➢Post mortem analysis of MEAs
- To facilitate the installation and replacement of a single PEMFCH a prototype long-life Modular multi-PEMFCHs system for Combined Heat and Power (MoPEM-CHP) is designed

### WP4 – Dissemination and exploitation of results

- Dissemination. Goal is to establish appropriate communication channels between the project consortium and external audiences.
- Exploitation. Strategy will put attention on potential markets, business models and management of IPR issues emerging during implementation of the project.

➤Exchange of Researchers and seminars/workshops.

# Strategies to improve the durability and the stability at T>100°C

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

For the membrane:

- <u>Thermal annealing</u>
- <u>Chemical crosslinking</u>
- 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

# WP 1. Long-life membranes for PEMFCH Most significant results

**Crosslinked SAPs (**SPEEK, SPEEK-WC, Fumion<sup>®</sup> ST310, Fumion<sup>®</sup> ST0305, Fumion<sup>®</sup> S60, Fumion<sup>®</sup> S340, Fumion<sup>®</sup> S204) membranes endured temperatures up to 140°C, reaching, in some cases, a conductivity of 0.07 S cm<sup>-1</sup> at 100°C and 95% RH.

(A)



We demonstrated that for PFSA membranes, the thermal annealed Nafion 212 is stable up to 120°C.

# Mass transport properties

# measurements





The mass transport properties measurements confirmed а high durability of membranes under stressed conditions. Globally, the SAP membranes showed significant higher fuel barrier (lower properties permeability) than native Nafion.

# 2. New concept of MEA with improved durability Most significant results

- •The electrocatalyst prepared in this project are very good, although the particle size of the nanoparticles is considerably larger. The larger size means higher stability regarding the particle growth at elevated temperatures
- •As a result of the electrodeposition process the degree of catalyst utilization is much higher: essentially all of electrocatalyst nanoparticles are in contact with both the ionically conducting ionomer and the electronically conducting electrode materials.





WP 3. Lifetime test and prediction techniques, establishment of accelerated test techniques. Most significant results

A protocol for MEAs characterization and accelerated tests has been elaborated and used for characterization at high temperature.



WP 3. Lifetime test and prediction techniques, establishment of accelerated test techniques. <u>Most significant results</u>

The bench system has been improved including the control system specifically operating on the temperature and relative humidify as required by the project and it has been utilized with some MEAs.

















# MOPEM



The MoPEM-CHP system has been designed and built to allow the easy replacement ("use and discard") of MEAs.

In addition, the system is designed to allow adiabatic operations maximizing the recovery of heat produced by cogeneration.

# Dissemination & public awareness

### LoLiPEM

Project

Consortium

Contacts

Consortium Meetings

Farrars 🕝 🕕 🌉

LoLiPEM

Events

News

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Publications

Download

Links

New Energy World

LoL.IPCM is a research project devoted to the development of new membranex, electrodex and a CHP module for station any power generation & combined heat and power (SIPC&CHP) systems, based on Polymeric Electrolyte Membrane Fuel Cel Histopen (IPCMP CH).

Search annar michain

(Brunck)

A PEMP CH operating in the temperature range of 100-130°C is highly desirable and could be declaive for the development of SPG&CHP systems based on PEMP CHs.

PEDISON Rematach

LoLi I<sup>®</sup>CM arms to operate in this temperature range above 100°C exceeding the state-of-the-art (10-80°C) which regressents the main charaback for the PSMF CH development.

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

The meno objective of the LoL //PAM project is to give a clear demonstration that long-ife SPGSCHE systems based on PEMP-CHalopensing above 1007 C can now be developed on the basis of recent knowledge on the degradation metoof incomer: membranes and on incovative synthetic approaches excertly disclosed by some periodperial of this project.

Some key points in the research activities are

 Development of long life (onger 40000 hours) perfusions without a word membranes and suitonated aromatic polymer membranes operating at a current density of at least 4000 A m

2. Development of long-life catalytic electrodes and Membrane Electrode Assemblies (MEAs)

1. Development of a grototype of a modular SI\*G&CHP system including more PEMP CHs built with the new long-life MEAs

4. The understanding of degradation mechanism, by means of accelerated aging tests and long-term single cell measurements, in order to predict the life-time 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 iterature 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 vincle modular system.

The project will benefit of the synergy ansing 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 development and testing.

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



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

# Deliverables of first 18th month

Del. no.	Deliverable name	Status
1.1	PFSA membranes	Delivered
1.2	SAP membranes measurements	Delivered
1.3	Set-up for permeation measurements	Delivered
2.1	MEAs suitable for temperature higher than 100°C	Delivered
4.1.	LoLiPEM project brochure	Delivered
4.2.	LoLiPEM website up and running	Delivered
4.3	Workshop on "Membrane Materials: Preparation and Characterization"	Delivered
4.4	Establishment of the strategy of exploitation	Delivered
4.5	Workshop on "Electrochemistry – Electrocatalysis"	Scheduled for March 2012, 25-27 <sup>th</sup>

no.	
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4.5	Workshop on "Electrocher Electrocatalysis"
5.1	Progress report
5.2	Progress report
5.4	Mid Term report (including management)

Deliverable name

Del.





- membrane cast from DMAc
- heat-treated at 180 °C / 15 h
- soluble in boiling water
- soluble in hot DMAc
- $\rightarrow$  No crosslinking in DMAc

- membrane cast from DMSO
- heat-treated at 180 °C / 15 h
- insoluble in boiling water
- insoluble in hot DMAc
- $\rightarrow$  Crosslinking in DMSO



no.	Denverable flame	
1.1	PFSA membranes	
1.2	SAP membranes me	asurements
1.3	Set-up for permeation	on
0.4	measurements MEAs suitable for te	Project
2.1	higher than 100°C	LoLIPEN is a re
4.1	LoLiPEM project bro	development of i and a CHP modu
• 4.2	LoLiPEM website up	generation & co (SPG&CHP) sys Electrolyte Memi (PEMFCH).
4.3	Workshop on "Mem Materials: Preparatio Characterization"	A PEMFCH oper of 100-130°C is i decisive for the o
4.4	Establishment of the exploitation	systems based o
4.5	Workshop on "Electr Electrocatalysis"	range above 104 state-of-the-art ( mein drawbeck f
5.1	Progress report	have several edv
5.2	Progress report	warm water distr
5.4	Mid Term report (ind	impurities in the
	management)	Mineuce, etc.

Dolivorable name

Del.

### Project

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PEMFCH operating in the temperature range 100-130°C is highly desirable and could be scisive for the development of SPG&CHP vstams based on PEMFCHa.

oLIPEM sime to operate in this temperature inge above 100°C exceeding the tate-of-the-art (70-80°C) which represents the ain drawback for the PEMFCH development. perating temperatures above 100°C would ave several advantages including easier arm water distribution in buildings, reduced node poisoning due to carbon monocide npurities in the fuel, improved fuel addiation netics, etc.

The main objective of the LoLIPEN project is to give a clear demonstration that long-life SPG&CHP systems based on PEMFCHs 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

2

3

- 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<sup>2</sup>
- development of long-life catalytic electrodes and Membrane Electrode Assemblies (NEAs)
- development of a prototype of a modular **SPG&CHP system including more** PEMFCHs built with the new long-life MEAs

- The understanding of degradation mechanism, by means of accelerated aging teets and long-term single cell measurements, in order to predict the life-time and give feedback to the developing of membranes and electrodes
- benchmarking of the performance 5 of a single-cell and the modular prototype against the best literature results.

The operating temperature of interest for the LoLIPEN project is in the range of 100-130°C for both new membranes, electrodee, MEAe 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.

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1.2	SAP membranes measu	urement	S									
1.3	Set-up for permeation measurements	🗳 Lol iPEM - Mo	zilla Firef	ox								
2.1	MEAs suitable for temp higher than 100°C	Plik Edycja Wio LoLiPEM	dok <u>H</u> istori www.lolipem.	a <u>Z</u> akładki <u>N</u> arzędzia + eu/project/	Pomo <u>c</u>					★ - C		- - - -
4.1	LoLiPEM project broch			Partners 🕞 🕻		ି 🕕 ଚା	DISON fumat	tech <b>C</b>		Search enter text here		
4.2	LoLiPEM website up an			Lol	_iPEM	LoLiPE	ЕM					
4.3	Workshop on "Membra Materials: Preparation Characterization"		F	Project Consortium Contacts	*	LoLiPEM is a researd power generation & Hydrogen (PEMFCH). A PEMFCH operating SPG&CHP systems I	In project devoted to the combined heat and po in the temperature rang pased on PEMFCHs.	e development of <b>new</b> wwer (SPG&CHP) sys ge of <b>100-130°C</b> is his	r membranes, electroo iems, based on Polym ghly desirable and coul	les and a CHP module for sta eric Electrolyte Membrane Fue d be decisive for the developn	<b>itionary</b> el Cell nent of	1
4.4	Establishment of the st exploitation			Consortium Me Events	etings	LoLiPEM aims to ope the main drawback fo Operating temperatu reduced anode poiso	rate in this temperatur r the PEMFCH develop res above 100°C would ning due to carbon mo	e range <b>above 100°C</b> iment. I have several advant inoxide impurities in t	exceeding the state-of ages including easier v he fuel, improved fuel o	the-art (70-80°C) which repre varm water distribution in buil xidation kinetics, etc.	sents dings,	
4.5	Workshop on "Electroc			News Publications		The main objective o PEMFCHs operating of ionomeric membra	f the LoLiPEM project i above 100°C can now l anes and on innovative	s to give a clear dem be developed on the l synthetic approaches	onstration that long-life basis of recent knowled recently disclosed by	SPG&CHP systems based or Ige on the degradation mecha some participants of this proje	n anisms ect.	
5.1	Progress report			Download		Some key points in th	e research activities ar <b>1g life</b> (longer 40000 ho	re: ours) <b>perfluoro sulfo</b> i	nic acid membranes a	nd sulfonated aromatic polyn	ner	
5.2	Progress report			LINKS		2. Development of lo	ig at a current density o ng-life catalytic electrod	if at least 4000 A m <sup>-2</sup> les and <b>Membrane El</b>	ectrode Assemblies (1	//EAs)		
5.4	Mid Term report (inclue management)			New Energy World	>	3. Development of a p 4. The understanding measurements, in or 5. <b>Benchmarking</b> of t	prototype of <b>a modular</b> of <b>degradation mecha</b> der to predict the life-tir he performance of a si	SPG&CHP system in anism, by means of a me and give feedback ngle-cell and the mod	cluding more PEMFCH ccelerated aging tests to the developing of m fular prototype against	s built with the new long-life M and long-term single cell embranes and electrodes the best literature results.	1EAs	
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# Deliverables of first 18th month

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4.4 4.5 5.1 5.2	Materials: Preparation Characterization" Establishment of the s exploitation Workshop on "Electroc Electrocatalysis" Progress report Progress report		

Del.



# Deliverable name PFSA membranes SAP membranes mea Set-up for permeation measurements MEAs suitable for ten higher than 100°C



Del.

no.

1.1

1.2

1.3



# Deliverables of first 18<sup>th</sup> month



# Intern. Workshop Electrocatalysis





St. Ingbert near Saarbrücken, Historical Steel Company ("Alte Schmelz") Sunday, 25 March 2012 Welcome reception Monday, 26 March 2012 Conference in the evening Conference Dinner Tuesday, 27 March 2012 Conference, end 13:00 h

Main topics: fuel cells, batteries, electrolysis, photoelectrocatalysis, bioelectrocatalysis

4.5	Workshop on "Electrochemistry – Electrocatalysis"
5.1	Progress report
5.2	Progress report
5 /	Mid Term report (including
5.4	management)

# 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 realization	achieved
M5	Modular multi-cell system design and realization	achieved
M6	Degradation and lifetime test	achieved
M7	Innovative MEA working above	Foreseen M24
M8	Cost of use and discard MEA	Foreseen M30
M9	Publications, patents, conferences	During the project activity

Milestones foreseen and achieved within 18th month-

Milesto		
ne	Milestone name	hydrogen pressure hydrogen temperature hydrogen temperature
no.		sensor sensor sensor sensor
M1	Kick off meeting	Inlet air Hydrogen humidity
N/12	PFSA membrane	pressure sensor
	stability ex-situ test	Air humidity
МЗ	SAP membrane	flow sensor
1415	stability ex-situ test	Sensor Stack Voltage
	Single PEMFCH	Air flow
M4	design and	sensor Stack current
	realization	
	Modular multi-cell	Monitoring, alarm control and steady-state
M5	system design and	target optimizer
	realization	► Relay
MG	Degradation and	Air flow
IVIO	lifetime test	controller
		Hydrogen flow controllerAir humidifier controllerHydrogen humidifier controllerStack temperature controllerAnode back pressure regulatorPotenciostat controllerCathode back pressure regulator

# Milestones foreseen and achieved within 18th month-

Milesto	
ne	Milestone name
no.	
M1	Kick off meeting
1.4.2	PFSA membrane
IVIZ	stability ex-situ test
N/10	SAP membrane
1013	stability ex-situ test
	Single PEMFCH
M4	design and
	realization
	Modular multi-cell
M5	system design and
	realization
MG	Degradation and
IVIO	lifetime test



# Where we are where we are going....



Status of the hydrothermal resistance of the thermal annealed Nafion membrane Status of the hydrothermal resistance of the thermal crosslinked SPEEK membrane



# Thank you for your attention