AGENCE NATIONALE DE LA RECHERCHE

ANR

Outline of granted projects in 2010
Programme " Hydrogène et piles à combustible "

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Call 2010

Project Title	**APHRODITE - HSTE stack under pressure with maximum contact area and gas distribution through the electrode**

Abstract

The Aphrodite project deals with hydrogen production by High Temperature Steam Electrolysis (HTSE). It aims at designing, manufacturing and testing a new concept of HTSE stack with high performances by operating at high pressure (30 bar). It is not only an innovative design but also a new approach for stacking the different elements, for sealing and for using gas pressure. To our best knowledge, this concept has no equivalent, and is the first HTSE planar stack under pressure. This industrial research project focuses on HTSE testing under pressure associated with modelling the thermal, electrochemical and mechanical response of the stack. For this, a study of electrochemical phenomena involved in high pressure for each electrode will be conducted as part of a thesis. Moreover, these models will be introduced in a simulation tool to analyze and size further tests.

The software platform from the MOISE project (ANR PAN-H 2007) will be used and expanded. A step by step experimental validation (Gas and current leads, tightness, integrity of cells during assembly ...) will be conducted prior to pressure testing in order to optimize the stack design. Seals will be metallic and innovative, coming from the project EMAIL (ANR PAN-H 2007). The pressure tests conducted at different scales (cell, single repeat unit and stack) will allow the understanding of phenomena involved in the HTSE under high pressure. These tests will also supply a validation of this process for massive hydrogen production.

The general approach for the project organization is to conduct in parallel :
- Action to enrich the knowledge of the HTSE under pressure.
- Manufacturing and testing of a first HTSE stack under pressure, based on an innovative concept devoted to a running under pressure.
- Quantification thanks to simulations of the performance gains (optimization of the surface, water use rate, performance of production, degradation ...) really obtained in the concept.

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ANR Grant	1176 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-001
Competitivenes Cluster	TENERRDIS

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**DIAPASON 2 - Diagnosis of Fuel Cells for stationary and automotive applications (2nd phase)**

Abstract

Fuel cell is a promising technology for both automotive and stationary applications. However, its reliability and its lifetime remain major hurdles for its wide access to these two markets. It is therefore necessary to develop reliable diagnosis tools with minimal instrumentation and even without any additional instrumentation to the one included in the systems. For that purpose, the DIAPASON project (ANR PAN-H 2006) aimed at developing different diagnosis methods for fuel cell, using only the stack as sensor and by comparing diagnosis methods based on physical or black box models or based on pattern recognition algorithms. DIAPASON project has already resulted in developing :

* an impedance spectrometer able to perform impedance spectras on stacks with voltages up to 500 V.

* diagnosis algorithms for detection of fuel cells' failures based on dynamic neural networks and a patented diagnosis method based on pattern recognition.

* a 24 channels cardboard measuring voltages through GMR (Giant Magneto-Resistance) that was interfaced with a multiplexing cardboard, that was itself controlled by a digitalization cardboard connected to a PC working under Labview and Matlab. This set-up was experimentally successfully validated.

* a Labview and Matlab interface between diagnosis algorithms with acquisition cardboard, able to diagnose fuel cell's state of health.

This project is a continuation of DIAPASON project and aims, in the same time, at bringing several major breakthroughs :

* new algorithms développement based on new innovative approaches (statistic methods or operating point follow-up).

* extension of the validity range of both the abovementioned approaches and of those already studied during the first phase (black box models and pattern recognition based algorithms) to other defaults that were not considered in phase 1.

* extension of present measurements possibility (now, only voltage with cycle time of 1.6 ms) to: shorter cycle times (~100 µHz for impedance measurements), other variables (current, pressure drops,...), higher power ranges (100 to 200 cells stacks).

* integration, with the help of the skills and know-how of a SME specialized in electronic components integration and project partner, all the modules developed in DIAPASON and improved in this project in a single hybride on-board module gathering GMR cells, instrumentation, calculation core and extern memory.
* integration of well known algorithms (FFT, ...) or developped during this project in the shape of IP software components, easily integrable in a chip.
These diagnosis techniques could then be used either in real time (by coupling with fuel cell's regulation system,
"On-board diagnostic") or during regular and planned maintenance operations. Such techniques will then allow improving fuel cell system's reliability and increasing its lifetime by anticipating degradation phenomenon.

In fine, this project will pay a special attention to the validation of the performances of the developed integrated (hardware + algorithm) diagnosis tool on two real systems, dedicated to automotive and microcogeneration applications. This tool will therefore represent a project's major expected breakthrough, that will in fine allow increasing the system's reliability and increasing its lifetime. It will also set and strengthen a solid know-how at national level, guaranteeing a rapid valorisation of project's results by fuel cell based systems users or manufacturers.

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ANR Grant	1440 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-002
Competitivenes Cluster	TENERRDIS

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**INEXTREMIS - In and ex situ link : water transport and distribution through the working ion exchange membrane**

Abstract

INEXTREMIS is a fundamental research project, exploratory type, which aims to contribute to the understanding of coupled charge/mass (proton/water) transport phenomena involved in the operation of polymer electrolyte fuel cells. That in order to establish relevant links between the evolution of the electrolyte water content and the electrochemical performances of the fuel cell.

Three complementary experimental methods, all based on radiation scattering, will be used for the determination of water concentration profiles through the thickness of the working electrolyte. Raman scattering is an up-and-coming technique for studying such problems, characterised by an excellent spatial resolution (few µm3). Small angle radiation scattering (neutrons and x-ray) have been successfully used to obtain water profiles through ionic polymers.

Neutron scattering measurements will be used as reference, to corroborate results obtained from x-ray and Raman scattering. It should be noted that, because of the limited accessibility to radiation sources, neutrons scattering can be employed usually only for specific, targeted, studies. This justifies the need to develop new in situ characterisation methods, less onerous from the implementation point of view.
The hydration state of the electrolyte during operation is highly heterogeneous. In this project, the distribution of water through the membrane thickness will be investigated at the same time as a function of the cell working conditions and at different locations in the heart of the electrochemical system.

Namely, at the membrane placed in the gas distribution channels as well as between the current collection ribs.
Among the expected outcomes of the project, we would like to emphasize the determination of local water diffusion coefficients (as a function of the local water content through the membrane thickness) and the electro-osmotic drag coefficients, for Nafion and Aquivion membranes. Furthermore, new membranes with hierarchical structure will be obtained from commercial ones. Their electrochemical properties will be investigated and in situ Raman analysis will allow evaluating the impact of the multilayer structure on the water repartition through the thickness.

Modelling and simulation of water transport in polymer membranes will be improved by using the experimentally determined water concentration profiles and diffusion coefficients (water diffusion, electro-osmotic drag). As a function of simulation results, the design of new membranes with hierarchical structure will be proposed. The efficacy of this strategy to improve water management in fuel cells will be verified by studying the behaviour of the first samples of multilayer materials obtained from Nafion and Aquivion.

INEXTREMIS is an exploratory project, including different research approaches: from the carrying out of new experimental set up until the modelling of transport phenomena and the shaping of new membranes. The detailed analysis of the highly coupled transport phenomena occurring in the heart of PEMFCs, strongly affecting the electrochemical performances of the system, needs the joining of several ex and in situ measurements, realized on or of fuel cell operation.

The approach proposed in this project is, therefore, not only to use emerging measurement techniques, which can give improved knowledge, but also to separate the whole physical phenomena involved through targeted, complementary experiments and methods.

The comparison of a wide amount of in and ex situ data will allow verifying whether or to what extent results obtained from measurements on membranes under equilibrium and homogeneous conditions can be useful to model the fuel cell electrolyte behaviour under working conditions. This is, in our opinion, the only realistic approach to establish relationships between the structural features of the electrolyte, its physical properties (especially hydration) and the experimental conditions.

Consortium	ENSCM/IEM CNRS/SPrAM/LSPAM CEA/DRT/LITEN
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ANR Grant	320 k€
Kick off and duration	January 2011 - 24 months
Reference	ANR-10-HPAC-003
Competitivenes Cluster	

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**MEMFOS - Fluoro-phosphonic Membranes for High Temperature Fuel Cells**
Abstract	MEMFOS project aims at developping a new synthetic strategy to afford, in the next few years, a newly formed polyelectrolyte membrane for fuel cell (PEMFC). This new PEMFC will perform for stationnay use as well as at high temperature (120°C or more). More precisely, unlike commercially available PEMFC, this membrane will be used in a wide range of temperature (from room temperature to 150°C) both with humid and dry gazes. This project will allow to overcome one of the main drawbacks in order to developp the PEMFC-based energy technology. Until now, no membrane is able to lead to high protonic conductivities both in a wide range of temperature (from room temperature to 150°C) and in a wide range of relative humidity (from dry to 100%). With the MEMFOS project we want to develop a new type of fluoro-phosphonic polymeric membranes giving rise of high conductivity values both in a wide range of temperature (from room temperature to 150°C) and in a wide range of relative humidity (from dry to 100%). A first generation of fluoro-phosphonic polymeric membrane has been already made by IAM (PhD 2006-09) by chemical modification of fluorinated polymers, obtained by radical polymerization. This first generation of polymeric membranes had been patented (three partners from MEMFOS project) and represents the "back up" of the MEMFOS project. The ionic exchange capacities obtained from these membranes range from 4 to 6 meq/g, leading to protonic conductivities of about 20 mS/cm (both at dry and 100% relative humidity).
Consortium	CEA ENSCM/IAM Univ Montpellier2/IEM HELION
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ANR Grant	745 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-004
Competitivenes Cluster	S2E2 (Sciences et Systèmes de l'Energie Electrique) ; TRIMATEC

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**PILE-EAU-BIOGAZ - Technical, economic and environmental feasibility of solide oxyde fuel cells (SOFC) for electricity generation from biogas**

Abstract

The ANR H-PAC 2010 call program (extract) "aims to contribute to the development of French industrial sector of fuel cells for stationary applications ..." expecting essentially four types of technical solutions, namely "the implementation of innovative materials more robust and reliable, the integration of components into new systems at competitive cost for the types of applications covered, the design and integration of systems including intelligent management of energy and finally evaluate the introduction of hydrogen & fuel cells in the energy management system (combined heat and power, management of renewable energy and distributed generation)".

In fact, SOFC is highly energy efficient, allowing high electrical efficiency (> 45%), much higher than those of gas turbines (15-25%) or internal combustion motors (20-30%). In addition, the SOFC can be supplied with various types of fuels other than hydrogen, including natural gas (rich in CH4) but also of biogas (mainly mixture CH4/CO2).

This biogas is an attractive source of renewable energy because it comes from the anaerobic digestion of biomass. When biomass is a fatal residue (i.e. sludge from sewage treatment plants or fermentable fraction of household waste), the environmental benefit is even greater. However, the requirement for pre-processing biogas sufficient for good performance of the SOFC stack is now unknown.

This research project proposes to demonstrate at real-conditions in a wastewater treatment plant the feasibility of coupling a treated biogas into a SOFC stack and identify the processing system for a minimum biogas treatment for the production of electricity and heat co-generation for stationary applications. The main deliverable of the project will be the on-site operation of a SOFC under biogas for a few hundred hours. This will include specifications that are necessary to overcome the presence of some minority biogas, such as sulfur or halogenated compounds, which can be particularly harmful for use in fuel cells.
To do this, new anode materials for tolerance to impurities will be proposed in this project as well as the biogas upgrading techniques well suited to such application to ensure the performance and sustainability of an SOFC operating on biogas.

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ANR Grant	1169 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-005
Competitivenes Cluster	TENERRDIS ; AXELERA

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**STHYME - Wet and affordable hydrogen storage**

Abstract

In the case of mass production of hydrogen by electrolysis from renewable energies, a hydrogen storage buffer is often needed. This one requires gas drying beforehand, indeed :
- in the case of metallic tank, drying is required to prevent corrosion,
- when hydrogen is stored as metal hydrides, a very dry hydrogen is required.

However, for PEM fuel cell the use of this drying is not necessary. Furthermore, for the combustion of hydrogen in a gas turbine in order to reduce the NOx emissions, a re-humidification of the hydrogen is commonly performed.

This drying operation is costly in energy and investment. In sizing the drying device at the right level, the project aims to significantly improve the energy efficiency of a hydrogen chain coupled to renewable energies and to reduce its cost.

Considering the different ways of storing hydrogen, such drying simplification is not easy, because :

(a) the materials used for storing and conveying hydrogen are low alloy steels sensitive to aqueous corrosion as well as to hydrogen embrittlement, and the interactions between these two types of damages have to be investigated

(b) if we consider a metal hydride storage system, gas moisture accelerates the aging of these hydrides which are very sensitive to hydrolysis,

(c) tanks with internal polymer liners have been designed for storing dry and high-pressure hydrogen. However in the case of wet hydrogen, the hydrolysis and aging behaviour of these liners are poorly known.

The STHYME project aims to simplify the drying for three ways of storage:
- for a pressure storage in a steel tank, by studying the impact of humidity on the corrosion and hydrogen embrittlement of the steel used, in order to design the drying at the correct level and thus to reduce its investment cost and to improve the global energy efficiency,
- for a storage under MgH2 hydrides, by analyzing the behaviour of the hydride at different level of humidity and by developing drying solutions, well adapted to hydride storage and able to re-wet the gas when desorbed, this without energy consumption.
- a direct and cost-competitive storage of wet hydrogen under medium pressure, possibly the outlet pressure of the electrolyser, thanks to the use of an internal liner polymer,

To carry out this project, we rely on strong partnership skills, in PEM electrolysis and fuel cell systems, in corrosion and hydrogen steel embrittlement, in polymer and in hydride storage system.
This partnership will help to develop an innovative drying system coupled with hydride storage system, to evaluate the influence of moisture on the hydrogen embrittlement and corrosion of steel pipe and to implement low cost storage solution, thanks to the use of an inner polymer liner.
In parallel we will rely on techno-economic analysis to guide choices toward solutions providing economic gain and / or energy saving at the system level.
Once the technologies developed, we will achieve for each storage routes, a small demonstrator coupling a PEM electrolyser with the drying solution well adapted to the storage system. Tests will be performed to evaluate lifetime, aging behaviour in order to better quantify the possible economic gains.

Consortium	CEA/LITEN HELION INPT/CIRIMAT McPHY
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ANR Grant	994 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-007
Competitivenes Cluster	TENERRDIS ; CAPENERGIES

Programme '' Hydrogène et piles à combustible ''

Call 2010

Project Title	**TOLEDO - Damage tolerance of compressed gaseous hydrogen composite vessels**

Abstract

The development of hydrogen as a reliable energy vector is strongly connected to the performance and level of safety of the components of the supply chain. In this respect, achieving an efficient storage is crucial to address transition markets and automotive markets. For near term, compressed hydrogen storage is currently the most promising technology.

Compressed hydrogen for industrial applications is stored at 200 bar in metallic cylinders which have poor mass storage efficiency but present high impact resistance. To achieve required performance in terms of autonomy and weight efficiency, hydrogen must be stored at pressure up to 700 bar in carbon fibers composites cylinders. However the damage resulting from a shock, its evolution during service and thus the cylinder tolerance to damage are not well described.

As a consequence, the design of the composites cylinders is conservative and even minor shock on cylinder results in the cylinder withdrawal from the supply chain, which affects the cost without an enhanced guaranty of safety.

In the scope of hydrogen energy markets, the cylinders can be subjected to a broad range of impacts either usual or accidental (car accident, during handling and transportation of transportable cylinders) and can be in the hand of people with no experience of compressed gas handling. It is thus critical to assess impact resistance of the storage and to determine which impact causes a cylinder burst immediately or after some time in service.

In addition, taking into account that some 2015 DOE performance targets are almost reached by composites cylinders and that there are on-going projects to improve manufacturing & materials, a study on damage tolerance of these structures (i.e. thick composites made by filament winding) is justified and would be complementary to current approach.

The development of scientific knowledge on the behavior of carbon fiber composites cylinder subjected to impacts and of numeric tools to predict residual performance of a cylinder in service presenting damage from a shock are the main objective of the project TOLEDO, submitted to the French call ANR H-PAC 2010.

The project gathers an industrial partner Air Liquide as an end-user of composites cylinders with experience on cylinder supply chain and safety, CEA who has cylinder testing facilities and cylinder design experience and two academic partners with complementary competences in impact generation, damage characterization and composites structure durability that are acknowledged by the academic world (LAMEFIP from ENSAM Bordeaux and Institut P' – ENSMA, Poitiers).
In the framework of TOLEDO program, a significant number of high pressure composites cylinders will thus be subjected to drop and shock tests representative of normal and accidental situations in the Hydrogen Energy supply chain and during handling by the customer.

Different techniques will be used to characterize the resulting damage on the composite structure. The criticality of the damage for the cylinder will be assessed by the study of residual performance of the cylinder after the impact and more importantly after further use (static and cyclic pressure load, effect of temperature).
This part of the study will involve tests on specimens, a numeric study and a validation on cylinders and will provide knowledge on lifetime predictions.
This approach will lead to recommendations for the industry and normative committees on the design of cylinders taking into account a quantitative analysis of damage tolerance and possible protections and for the control of cylinders in service by providing knowledge to define a withdrawal threshold.

Consortium	Air Liquide CEA Arts et Metiers ParisTech-LAMEFIP ENSMA/P'
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ANR Grant	1077 k€
Kick off and duration	January 2011 - 36 months
Reference	ANR-10-HPAC-006
Competitivenes Cluster	S2E2 (Sciences et Systèmes de l'Energie Electrique)