Advanced m-CHP fuel CELL system based on a novel bio-ethanol

Fluidized bed membrane reformer

FLUIDCELL

Editorial
Many progresses have been achieved since we start the project 18th months ago. New stable and active catalyst have been produced and tested. On the other side, the dependence of the H2 permeance and H2/N2 permselectivity on the selective layer thickness has been defined for ultra-thin Pd-Ag membranes (0.5 -1.3 µm). Besides, a kinetic model for the ethanol autothermal reforming has been developed being validated with experimental results. Membrane reactor has been tested under pure permeation conditions as well as under reaction. In the meanwhile, the pilot reactor prototype has been designed and two different membrane reactor designs have been considered and optimized in a m-CHP system to evaluate the optimisation of the fuel cell compared to a reference case. Besides, collaboration has been established with other major European Project funded on membrane reactors.

More info could be found in our website www.fluidcell.eu.

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What is FLUIDCELL?

Concept

The FluidCELL project aims at developing an advanced m-CHP fuel cell system for decentralized off-grid applications. The new m-CHP will be based on a novel bio-ethanol fluidised bed catalytic membrane reformer and the most advance technology at the fuel cell level. Taking advantage of, a) bio-ethanol, representing a non-toxic, high energy density, easy handling and commercially available worldwide as a renewable energy supply, b) the fuel cell, that combines high efficiency, low emissions, and low noise, and finally c) Catalytic Membrane Reactor (CMR) achieving high hydrogen conversion rates, lower working temperatures and smaller physical footprint, FluidCELL targets giving an answer to the large number of off-grid decentralized energy consumers that actually depend on expensive and high polluting sources such as LPGs, bottle gas, heating oil or solid fuels.

![Figure: Schematic of FLUIDCELL concept](image)

Target

The general objective of FLUIDCELL is to prove the concept of a novel bio-ethanol catalytic membrane reformer based micro-CHP system for decentralized off-grid applications while reducing the system cost from the state of the art to achieve cost below 5000 €/kW\text{el} in mass production.

The target is a net electric efficiency higher than 40% using bioethanol and an overall efficiency higher than 90%.
**Project objectives**

FluidCELL aims at developing a high efficient m-CHP system based on: i) design, construction and testing of an advanced low temperature bio-ethanol membrane reformer for pure hydrogen production with optimization of all the components of the reformer (catalysts, membranes, heat management, etc) and ii) the design and optimization of all the components for the integration of the system including the Fuel Cell Stack and its assembly (Reformer and Fuel Cell).

This general objective is directly related to the development of the novel catalytic membrane reactor (CMR) for hydrogen production with:

- Improved performance (high conversion at low temperature for the autothermal reforming reaction)
- Enhanced efficiency (electrical efficiency of > 40 % compared to conventional 34 %)
- Lifetime ambition (>40,000 hours) under CHP system working conditions
- Extremely reduced CO2 emissions compared to conventional fossil fuels.
- Good recyclability of its individual components and safety aspects for its integration in domestic CHP systems
Scientific and Technical challenges

The technical objectives on component level needed to achieve these goals with the bio-ethanol Catalytic Membrane Reformer based m-CHP system are the following:

- Application of advanced, active and selective, catalysts under moderate (< 500ºC) conditions and reduced cost.
- Application of new hydrogen permeable membrane materials with improved separation properties, long durability, and with reduced cost, to be used under reaction conditions.
- To assess the large-scale production of the membrane development.
- Understand the fundamental physico-chemical mechanisms and the relationship between structure/property/performance and manufacturing process in membranes and catalysts, in order to achieve radical improvements in membrane reactors.
- To design, model and build up novel more efficient (e.g. reducing the number of steps) bioethanol catalytic membrane reactor configurations based on the new membranes and catalysts for small-scale pure hydrogen production (3.5 Nm³/h of hydrogen).
- To validate the new membrane reactor configurations, and design a semi-industrial Reforming prototype for pure hydrogen production (3.5 Nm³/h).
- To improve the cost efficiency of membrane reactors by increasing their performance, decreasing the raw materials consumption and the associated energy losses.

Partnership

The FluidCELL consortium gathers 9 organisations from 6 Member States (France, Italy, Netherlands, Portugal, Spain and Switzerland). With 2 research institutes (CEA and TECNALIA), 4 universities (POLIMI, UNISAL, FEUP and TU/e), 2 SMEs (QUANTIS and HYGEAR) and one large company (ICI).
Project structure

The project is structured and divided into ten well-defined objective-oriented work packages following the focus on efficiency improvement of the overall m-CHP system.

FLUIDCELL in progress

The latest new on different WP activities are now reported:

Industrial specifications of Fuel Cell CHP system

A review of systems for simultaneous production of useful heat and electricity (Combined Heat and Power, CHP) is investigated. The focus is on devices with an electrical power output up to 50 kW, defined micro-CHP systems, according to the definition given in Directive 2004/8/EC. The field is further restricted to devices suitable for home installation and only a small fraction of products satisfy this constrain. This activity was completed and provided a full set of specification for FLUIDCELL to be considered in the system development.
Novel catalytic Formulations

UNISA explored some catalytic formulation, supported on cerium-oxide that was found an interesting support for various metals, since it

- significantly increases the H₂ yield;
- strongly favours the acetaldehyde route to COₓ and H₂ instead of its decomposition into CO and methane, due to the fast oxidation of the CH₃ groups of acetaldehyde, related to the well know oxygen storage capability and mobility of the support;
- favours the direct decomposition of water into hydrogen and not only into OH groups;
- inhibits the dehydration route to ethylene, that is a coke precursor, and promotes CHₓ oxidation and surface cleaning along the steam reforming process. For this reasons, the catalysts stability is improved.

UNISA was involved in the preparation of diverse catalysts, basing on this literature review and previous experience in the reforming processes. The first samples of catalyst supports (CeO₂ and CeO₂-ZrO₂) with different mean diameters were tested in the first decade of July in TU/e laboratories, with the aims to verify their fluidization in the bed reactor there available, and possible interactions with the membranes. The results of these tests highlighted the non-optimal fluidization of these supports as such: so other supports with high values of SSA, on which deposit CeO₂ or CeO₂-ZrO₂ and then the active species will be used. The supports that can be considered are: SiO₂, ZrO₂-SiO₂, γ-Al₂O₃, lanthanum-modified alumina. The second generation catalysts were prepared after the fluidization tests performed at TU/e on more fluidizable supports, such as SiO₂. After the positive results of these tests, UNISA started the preparation of the new catalysts by wet impregnation using SiO₂ in powder as fluidizable support, on which CeO₂ and then the active species were deposited. The precursor salts of active species are acetate for Ni, chloride for Pt and nitrate for CeO₂.

The prepared catalysts were characterized by means of several techniques. The experimental campaign to study the new prepared catalysts performance in the ESR reaction at T< 500 °C will be focused on the analysis of the effect of key operational parameters (such as steam-to-carbon, dilution, temperature, space velocity) on the catalyst performance, in terms of activity, selectivity and stability.

Some activity tests have been performed using the first samples of the Pt/Ni second generation catalysts, based on silica (SiO₂) in powder as mechanical supports, and Ceria (CeO₂). The results of these tests were very interesting in terms of catalytic activity towards the ethanol steam reforming reaction at low temperature.
Novel Membrane development

TECNALIA is developing Pd based membranes with high H\textsubscript{2} permeance and selectivity, and durability under conditions of bioethanol reforming MR in a fluidization regime (<500ºC). Several ultra-thin Pd-Ag membranes (0.6 – 1.3 µ) onto alumina tubular porous supports (100 nm pore size, Ø10mm) were prepared by simultaneous electroless plating deposition. The thickness of the membrane was controlled by changing the plating time. It was found that the H\textsubscript{2} permeation decreases and the H\textsubscript{2}/N\textsubscript{2} selectivity increases as the thickness of the membrane increases (Figure 1). The 1.3 µm thick Pd-Ag membrane was tested at 400 ºC for 1000 h (Figure 2). After few hours of activation the hydrogen permeation achieves a stable high H\textsubscript{2} permeance (1.0 x 10\textsuperscript{-5} mol m\textsuperscript{-2}s\textsuperscript{-1}Pa\textsuperscript{-1}) and good H\textsubscript{2}/N\textsubscript{2} selectivity (1900). The highest H\textsubscript{2} permeance reported with this selectivity onto Pd-based membranes developed by one step direct deposition.

![Figure 1. H\textsubscript{2} permeance and H\textsubscript{2}/N\textsubscript{2} selectivity versus thickness](image)

![Figure 2. Long term test on the 1.3 µm thick Pd-Ag membrane (400 ºC).](image)
Lab scale bio-ethanol catalytic membrane reformer

The work in the last months focused on the development of a kinetic model for the ethanol autothermal reforming, the study of membrane stability in fluidized bed and the design of a novel reactor for the lab scale test of the ethanol reforming reaction. After the new kinetics has been evaluated, the model has been validated with the experimental results, which consists on feeding different composition of EtOH/H2O/N2 and EtOH/H2O/Air/N2. The experimental results and the kinetics laws have been compared with some literature data and the kinetic model will be implemented in the fluidized bed membrane reactor model for the analysis of the entire system.

The membrane reactor was tested in pure permeation conditions as well as under reaction to determine the characteristics of the membranes as well as the performances of the overall system. The permeation test are based on feeding H2 and N2 at different pressure and the check of the flow rate at the permeate side. Results showed that the selectivity of the membrane is in the range of 5000-35000 depending on the operating pressure and that most of the leakage is concentrated in the sealing part. The reactive tests have been carried out both for methane reforming and ethanol reforming using different S/C and O/C.

Then, the membrane reactor was fed with ethanol – water mixture at different concentrations. Ethanol conversion and hydrogen permeation were evaluated at different pressures (from 1 bar to 3.5 bar) and different S/C. Complete conversion of ethanol to gas has been detected in the whole range of operating conditions.

In the figure below typical results of the ethanol reforming are reported.

![Figure 3: Performance for the Ethanol Auto-thermal reforming](image)
Design and Manufacturing of novel bio-ethanol catalytic membrane reformer

In 2015 the project started the phase of pilot scale prototype. The ongoing activities focus on the design of the core component of the fuel processor: the autothermal reforming membrane reactor. The goal of the design is to achieve the 3.5-4.0 Nm$^3$/h required for the fuel cell. The design conditions of the membrane reactor are 11 bar at 500 °C. The installed membranes are 40 cm long. The reactor uses steam as sweep gas in order to enhance the hydrogen permeation through the membrane. Therefore, the reactor will produce a stream of wet hydrogen which then needs to be cooled down and the condensed water drained.

In parallel the balance of plant (BOP) for the fuel processor is being designed. The fuel processor will be tested at HyGear starting during the first half of 2016 for following integration with the fuel cell and recovery heat exchangers at ICI’s facilities in Verona - Italy.

Fuel Cell Stack

Extensive range of conditions have been defined with the consortium with regard to reformer developed and to system application specifications. Sensitivity studies were conducted on a short stack (8 cells) made with reformate type reference MEAs. Tests showed influence of fuel composition, like performance losses due to presence of some carbon monoxide in the hydrogen produced. Dead end operation has been tested to check stack voltage compared to fuel circulating mode. Single cells tests conducted also with reference MEAs have shown, after some adaptation of the testing device, similar performance as same MEAs in stack. Simulation of single cell behaviour is conducted to help defining best suited components to be tested for selection. Single cells will be used for additional studies or benchmark about components and operating conditions effect. Stack testing will be conducted for better knowledge of the fuel cell behaviour in the relevant conditions, with possibly other selected components, and also including specific use of data for the validation of the model developed to describe the whole system operation.

Integration and Proof of Concept of m-CHP system

After the definition of the reference cases to compare the improvements of the novel CHP system with conventional fuel processors, the evaluation of the performances of FluidCELL concepts was carried out. Two different membrane reactor designs were considered and optimized: the first one adopts a sweep-gas stream, the second one a vacuum pump. The former allows higher system electric efficiency, while the latter requires less complex membrane reactor design, but the adoption of an expensive and power
consuming component as the vacuum pump. Net electric efficiency and membrane area for the different lay-out and operating conditions are summarized in Figure 4.

![Figure 4 Layouts comparison: electric efficiency and membranes area (Sw= Sweep, VP= vacuum pump, W/Et= Water to ethanol)](image)

As a term of comparison, the net electric efficiency of the reference case is 34.2%, therefore the adoption of the membrane reactor allows an efficiency increase of about 6% points.

**LCA and Safety analysis**

The objectives of the LCA and Safety analysis for the period are focused on analysing more in detail the results of the preliminary environmental Life Cycle Assessment calculated during the previous period. Quantis worked in collaboration with the partners to i) update the LCA according to the new modelling performed in W8.2 by POLIMI, and ii) identify the key parameters that influence the environmental impacts (e.g., electric efficiency, bioethanol dilution, dimensioning of the m-CHP, membrane area, etc...). The next step is then to work together with the partners to establish and evaluate different scenarios based on those parameters, in order to optimize the system from an environmental point of view.

As a reminder, the screening LCA results showed that the FluidCELL developed technology can be a better or worst environmental alternative than those existing conventional technologies and depends on the environmental indicator considered. The FluidCELL concept is always the best or among the best PEM fuel cell micro-CHP alternatives, except for the impacts on human health for which the impacts of the reformer catalyst are very high and inverse the trend.
FLUIDCELL consortium at the third progress meeting in Politecnico di Milano

On September 2015, Politecnico di Milano hosted the third partnership biannual meeting at the offices in Milan

**Mid-term exploitation workshop**

A mid-term exploitation workshop was held at the premises of Tecnalia. European Research projects generally perform well in developing new technologies and bringing forward innovations but they frequently do not fully use their potential and capacity to exploit, because adequate consideration is not given to non-technical issues such as protection of results, IPRs, exploitation rights, marketing, regulations and standards, partnership, financing, etc.

An exploitation workshop was carried out in order to identify non-technical factors, which could represent a risk that future results of the project would remain unexploited and to achieve a common understanding about IPRs and exploitation.

An exploitable result is that which has a commercial or social significance (i.e. provide knowledge or economic profit). In FluidCELL these are not limited to the complete FluidCELL system, therefore the consortium needed to identify new applications for “sub-systems” developed in the project (e.g. membrane separator, CHP controller, etc).

The workshop included sessions for addressing the following areas:

1. Identification of exploitable results
2. Intellectual Property Rights and Exploitable Claims situation
3. Risk assessment and management

The results from the analysis will be reported in the Plan for Use and Dissemination of Foreground (PUDF).
Highlights

12th International Conference on Catalysis in Membrane Reactors ICCMR12
22-25 June, Szczecin, Poland

FLUIDCELL project was presented during the session on European Projects that will be held on 23rd June 2015 (TBC). For further information on the programme and the registration, please visit the ICCMR12 website http://www.iccmr12.zut.edu.pl/.

Oral Presentations on FLUIDCELL achievements:


Poster on FLUIDCELL achievements:


Dissemination activities, publications and presentations:

- FLUIDCELL public presentation available on the website http://www.fluidcell.eu/content/presentations
### Upcoming events

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<th>Event Date</th>
<th>Event Details</th>
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<tr>
<td><strong>11 - 14 October 2015</strong></td>
<td>6th WHTC World Hydrogen Technology Convention, Sydney, Australia</td>
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<td><strong>19 - 21 October 2015</strong></td>
<td>International Conference on Hydrogen Safety, ICHS, Yokohama, Japan</td>
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<td><strong>1 - 3 November 2015</strong></td>
<td>12th MST2015, International conference on membrane science and technology, Teheran, Iran</td>
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<td><strong>16 - 19 November 2015</strong></td>
<td>Fuel Cell Seminar &amp; Energy Exposition 2015, Los Angeles, California</td>
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<td><strong>11 December 2015</strong></td>
<td>REFORCELL final dissemination event, Vaulx-Milieu, France</td>
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<tr>
<td><strong>16 - 18 December 2015</strong></td>
<td>6th European Fuel Cell Technology &amp; Applications Piero Lunghi Conference EFC15, Naples, Italy</td>
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<td><a href="http://www.europeanfuelcell.it/">http://www.europeanfuelcell.it/</a></td>
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<tr>
<td><strong>15 - 19 May 2016</strong></td>
<td>PERMEA 2016 - Membrane Science and Technology Conference of Visegrad Countries, Prague, CZ</td>
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<td>International conference MELPRO 2016 - membrane and electromembrane processes, Prague, CZ</td>
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<td><strong>13 - 17 June 2016</strong></td>
<td>21th WHEC World Hydrogen Energy Conference, Zaragoza, Spain</td>
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FLUIDCELL in figures:

- 9 partners (6 RES, 1 IND, 2 SME)
- 6 countries
- 4.2 M€ project (2.4 M€ EU funded)
- Start April 2014
- Duration: 36 months
- Key milestones:
  - December 2015 - Pilot scale prototype ready
  - April 2016 – Selection of fuel cell stack
  - August 2016 - Testing of the m-CHP system

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More information on FLUIDCELL (including a non-confidential presentation of the project) is available at the project website: http://www.fluidcell.eu

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Disclosure:
The present document reflects only the author’s views, and neither the FCH-JU nor the European Union is liable for any use that may be made of the information contained therein.
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Summary:

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FLUIDCELL brochure