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

Fluidized bed membrane reformer

FLUIDCELL

Editorial

Welcome to the new release of the FluidCELL newsletter. After two years, the FluidCELL project shows a big progress. Catalyst for the prototype has been prepared. New plating system for preparing long Pd-Ag membranes has been built and the first batch of 50 cm long membranes have been developed. The first experimental campaign of membrane reactor has been completed and the effect of the pressure at the feed side and the operating temperatures on the reactor performances has been evaluated and compared to the modelling. In the meanwhile, the prototype reactor is being constructed and assembly following the design of the membrane reactor that was completed by end of 2015. On the other side, work conducted on the fuel cell allowed to complete the information about the fuel cell components and fuel cell stack performance in the ranges of operating conditions of interest for the system development. Finally, a Life Cycle Perception game specific to the FluidCELL system has been developed by Quantis for improving the knowledge of the consortium on life cycle analysis. More info could be found in our website www.fluidcell.eu.

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Learning about LCA playing a game – Quantis Style

The Life Cycle Perception game (LCP™) is a business game designed by Quantis to learn about life cycle thinking through dynamic dialogue and demonstration. It compares personal perceptions of a products or a process' environmental, social and economic performance to the actual results of an LCA.

A LCP™ specific to the FluidCELL system has been developed by Quantis for the latest consortium meeting based on the LCA results calculated during the project. The objective of the 2 hour session was i) to engages project partners and leverage their curiosity about the FluidCELL system environmental impacts, and ii) to identify actions that could potentially reduce the impacts.

The LCP game consisted of four main steps:

1) **Organize the life cycle of the FluidCELL system** (2 separate teams)
   a. The 2 teams brainstormed on the life cycle of the FluidCELL system (What is needed to build the m-CHP plant? What is needed to operate it? Where does the end-of-life treatment take place? What about the additional boiler production?)
   b. Then, they placed cards around the main circle on the game board to illustrate this life cycle.

2) **Distribute the environmental impacts** (2 separate teams)
a. Tokens were placed on the game board to distribute the impacts among the main life cycle stages identified, for three different impact categories: impact on climate change, water withdrawal and impacts on human health (e.g.: Is the bioethanol production corresponding to higher impacts on climate change than the production of the reactor?);

b. Challenging time! The 2 teams had then to present and defend their life cycle and impact distribution to each other.

3) **Compare perception and actual LCA results** (all together)
   a. The actual LCA results were given, turning the center of the game board, in order to identify and explain the perception gaps;
   b. After those three steps, the environmental impacts of the FluidCELL system were well understood by the team!

4) **Identify potential impact reduction actions** (all together)
   a. Brainstorm and note all reduction ideas on post-its;
   b. Place all the actions identified on a decision matrix with one axis representing the impact reduction evaluation and the other axis the ease of implementation that is combining technical feasibility and costs.

In general, the game allowed a very good collaboration and a lot of interactions between all the partners. The first three steps brought a better awareness and a deep understanding of the environmental impacts of the FluidCELL system. Regarding the 4th step, all the partners took part and brought great ideas! And together, we identified several reduction actions and selected a few of them. The next steps are now to calculate and quantify the actual environmental impact reduction.

Thanks to all the partners for the participation and the very good collaboration!
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 1: 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 €/kWₐₑ 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).

![System schematic layout](image)

**Figure 2: System schematic layout**

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

**FOLLOW US ON LINKEDIN in membrane reactors group:**
https://www.linkedin.com/groups/8513530
Diary book: An italian in Grenoble

“Be sure, take with you very warm clothing because the winter in Grenoble is cold and snowy” was the suggestion of a friend few months ago, when I was preparing my luggage. Destination: CEA research center in Grenoble, which is entirely devoted to the development of renewable energy sources. The target of the six-months internship is the experimental characterization of PEM fuel cells behavior and their impact on the performances of the overall system developed in FluidCELL.

Grenoble is very attractive for scientists and researchers: there are many universities and research centers concentrated in a relatively small city. But Grenoble is very attractive also for mountain lovers, in fact the French call it “capitale des Alpes”. Around the city there are three main upland areas (Belledonne, Chartreuse, Vercors) with beautiful peaks, landscapes and many popular sky resorts. In general, mountain-related activities like skiing and trekking, or outdoor sports like running and cycling are very popular. The link between the city and the mountains is evident also inside the laboratory I work in: the test benches for the fuel cells stacks are named as the mountains around the city. I work on Obiou test bench, others are Taillefer, Gargas, Sirac. In general, I was surprised by the sportiness of inhabitants of Grenoble: for instance, many people move and go to work by bike, also when the weather is rainy, something inconceivable in Milan.

The past winter was not cold and snowy as I expected, so I never used cap and gloves, but I enjoyed the warm and sunny Sundays running on the track along the levee of the Isère River. On one hand I liked the warm temperatures, on the other hand it makes me think about the climate change and the importance to work on new “green technologies” and make them available as soon as possible. Now only few days are left to the end of my experience here, and I can wrap up: on the working side I learned a lot on PEM fuel cells and experimental techniques thanks to the experience of the people of the lab; on the personal side I discovered a city on a human scale, where it is nice to live in; finally on the “to do list” I add an idea for the next summer vacations: a trekking up to the top of Obiou!

Stefano
LATEST NEWS FROM THE PROJECT:

Novel catalytic formulations
UNISA investigated the activity and selectivity of different catalytic formulations. However, the most promising sample, in terms of catalytic performances and mechanical resistance under fluidization conditions, was a bimetallic (Pt-Ni) catalyst supported on a CeO₂-SiO₂ system. The Pt-Ni/CeO₂ catalyst deposition on SiO₂, in fact, improved ceria as well as active species dispersion, thus resulting in a better specific selectivity with respect to ceria-free catalysts. In particular, the main parameter to be optimized in terms of catalytic formulation was the CeO₂/SiO₂ ratio. Catalysts were prepared at different ceria content and tested for stability evaluation at 500°C, S/E=4 and O₂/E=0.5. All the samples showed very low carbon formation rates (2 or 3 order of magnitude lesser than the values obtained at the same operative conditions by other authors). However, the most promising catalyst was the 3wt%Pt-10wt%Ni/30%CeO₂/SiO₂, which also displayed a minimum in the Ni crystallite dimension (d_Ni). In fact, UNISA evaluated the relationship between coke selectivity and d_Ni, finding that the largest Ni particles caused high carbon formation rate.

Moreover, UNISA was involved in the manufacturing of the filler (7 dm³) + catalyst (2dm³) material for the tests in the pilot reactor. Figure 3 and Figure 4 report some steps of catalyst preparation. The solid, as scheduled, were sent to HYGEAR by M24.

![Figure 3: Samples after drying post CeO₂ (a), Ni (b) and Pt (c) impregnation.](image)

![Figure 4: Samples after calcination post CeO₂ (a), Ni (b) and Pt (c) impregnation.](image)
Novel Membrane development

TECNALIA is developing Pd based membranes with high H₂ permeance and selectivity, and durability under conditions of bioethanol reforming MR in a fluidization regime (<500ºC). For scaling up the membranes for prototype a new plating system has been constructed. This system has been recently used for preparing the first batch of 50 cm long Pd-Ag membranes (3-5 microns thick) supported on alumina tubular supports (100 nm pore size, Ø10mm) by simultaneous electroless plating deposition (Figure 5).

Figure 5: First batch of ceramic supported membranes for pilot scale membrane reactor (50 cm long).

Pd pore filled (PF) membrane are expected to be stronger under fluidization conditions. Besides, the Pd content is a fraction of the conventional membranes at the same thicknesses. PF membranes, using YSZ-Al₂O₃ (30 and 50% YSZ content) for the ceramic porous structure in which the Pd is filled, were tested at 300-550 °C. The membranes showed low N₂ permeation but their H₂ permeation is lower than expected.

Lab scale experiments

In the last period, different experiments have been carried out in both a small scale (single tube) and multitubular fluidized bed membrane reactor with the aim of model validation. In the following figures a comparison between the experimental results and the model results are reported.

The feeding conditions (based on equivalent ethanol as discussed in our recent paper) are reported in Table.

<table>
<thead>
<tr>
<th>composition</th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>5.2%</td>
</tr>
<tr>
<td>CO</td>
<td>5.2%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0%</td>
</tr>
<tr>
<td>H₂</td>
<td>5.2%</td>
</tr>
<tr>
<td>H₂O</td>
<td>31.4%</td>
</tr>
<tr>
<td>N₂</td>
<td>52.9%</td>
</tr>
</tbody>
</table>
Effect of the pressure at the feed side
The first comparison is related to the effect of the operating pressure at the feed/retentate side.

![Graph of retentate component fraction vs pressure](image1)

Figure 6: a) gas composition at the retentate side. T = 550°C and u/u_{inf} = 6; b) Permeated H2 through the membrane at different pressure

In Figure 6a, it is possible to see the composition of the retentate gas. The experimental and modelling results are similar. The error in the H2 vol. fraction is between decreases from 13% to 1.7% depending on the operating pressure. The results in the composition are obviously influenced by the H2 permeation: based on Figure 6b. By increasing the feed pressure the permeated H2 increases especially accordingly from the model results, but from the experimental results the permeated H2 slightly increases.

Effect of the temperature

In Figure 7, the comparison of modelling and experiments is carried out at different operating reactor temperature. By decreasing the temperature from 550°C (left in the figure) to 450°C the (right) the difference in the retentate gas composition and the corresponding permeated H2 becomes almost negligible.

![Graph of retentate composition fraction vs pressure](image2)

Figure 7: retentate composition (from experiments and modelling) at different temperature and pressure working with u/u_{inf} = 6. Starting from left 550°C, 500°C, 450°C
Design and Manufacturing of novel bio-ethanol catalytic membrane reformer

In the second year of the project the activities around the pilot scale fuel processor are focused on construction and assembly. The design of the membrane reactor was completed in 2015, and by the end of the year, assembly was already started. The objective of the ongoing activities are the assembly of the fuel processor into a compact skid including reactor and its balance of plant and controller. The membrane reactor contains 37 tubular Pd-based membranes of 40 cm length. Hydrogen permeation through the membranes is enhanced by the use of steam as sweep gas on the permeate side of the membranes.

The catalyst for the reactor has already been prepared. When the assembly of the reactor comes to conclusion, 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.

Figure 8: Sketch of the Fluidcell prototype
Fuel Cell Stack

During last period, work conducted on the fuel cell allowed to complete the information about the fuel cell components and fuel cell stack performance in the ranges of operating conditions of interest for the system development. Most of this activity was carried out by Stefano Foresti (Ph.D. student at Politecnico) at CEA lab.

Benchmark of Membrane Electrode Assemblies components has been conducted with single cell testing and modelling has been used for further interpretation. Impact of Gas Diffusion Layer and catalyst loadings have been considered, checking the impact on performance in the operating conditions relevant for the system.

Testing of short-stack has been performed in collaboration with WP8 in order to qualify the performance of the fuel cell in conditions related to various cases considering fuel processing and system operation. A short stack of 8 cells including local in-situ measurements for further information has been extensively tested with different sets of conditions (like gases pressures) and different fuel compositions simulating outputs from the reformer in carbon monoxide or inert gases content without or with air bleeding. The data have allowed to validate system model and to estimate the impact of fuel purification process and the impact of losses in the hydrogen quality onto the overall efficiency of the system depending on the selected scenario. Examples of I-V curves at different CO/H2 and inerts/H2 concentrations are reported in Figure 9 together with two cathode pressures (1.2 bara and 1.1 bara).

**Figure 9:** I-V curve measured at different fuel compositions and cathode pressures
Integration and Proof of Concept of m-CHP system

After the definition of the final prototype layout, based on sweep configuration, the activities during last period have been focused on:

- investigation of system off-design operation, in case of damages of the membrane reactor, with consequent impurities in the permeated hydrogen. In particular, a prediction of system performances in a wide range of condition have been analysed matching experimental results, achieved in WP7, and simulation.

- investigation of BoP components, in order to get the integration of the fuel processor with the stack ready. Costs, performances and materials have been taken into account, providing possible solution to deeply analyse during next period, in order to identify the suitable size among the solution available for each component.
Hi

Highlights
Fluidcell’s shufflin' through membranes
But our heads're in Zaragozza

- Advanced m-CHP fuel cell system based on a novel bio-ethanol fluidized bed membrane reformer – Oral presentation
- Three-dimensional modeling of liquid water transport and CO poisoning in a PEMFC operating on reformate - What’s the status?
- Palladium based membranes and membrane reactors for hydrogen production and purification – Oral presentation
- PEM fuel cells stack protection from CO-poisoning in a m-CHP system with membrane reformer – Oral presentation

http://www.whec2016.com/

In addition, Fluidicell will be attending the 11th Conference on Sustainable Development of Energy, Water and Environment Systems – SDEWES Conference, to be held in Lisbon in 2016 and ICIM conference that will be held in Georgia (USA) on 10-13th July.

- Fluidized bed membrane reactors for hydrogen production using thin Pd-based (<5 µm) supported membranes (ICIM 2016)
- Preparation and characterization of ceramic supported ultra-thin (~1 µm) Pd-Ag membranes (ICIM 2016)
- Achievements of EU projects on membrane reactor for hydrogen production (11th SDEWES)

Dissemination activities, publications and presentations:

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

8 – 11 May 2016  ICH2P-2016, International Conference on Hydrogen Production, Hangzhou, China  
http://ich2p-16.csp.escience.cn/

15 – 19 May 2016  PERMEA 2016, Membrane Science and Technology Conference of Visegrad Countries, Prague, Czech Republic  
http://www.melpro.cz/

22 – 25 May 2016  10th CITEM2016, Ibero-American Congress on Membrane Science and Technology, Mexico City, Mexico  
http://www.smcytm.org.mx/congreso/index.html

13 – 17 June 2016  21st WHEC World Hydrogen Energy Conference, Zaragoza, Spain  
http://www.whec2016.es/

15 – 17 June 2016  7th International Bioenergy Conference and Exhibition, Prince George, Canada  
http://www.bioenergyconference.org/

26 – 30 June 2016  ASME 2016 10th International Conference on Energy Sustainability  
ASME 2016 Power Conference  
Charlotte, North Carolina, USA  
https://www.asme.org/events/power-energy

6 – 7 July 2016  6th BIT, Annual World Congress of Bioenergy, Kintex, South Korea  

10 – 13 July 2016  14th ICIM2016, International Conference on Inorganic Membranes, Atlanta, USA  
http://www.icimconference2016.com

12 – 14 July 2016  Bioenergy 2016, Washington DC, USA  
http://www.ceref.org/bioenergy-2016

29 – 31 August 2016  2nd International Congress & Expo on Biofuels & Bioenergy, Sao Paulo, Brazil  
http://biofuels-bioenergy.conferenceseries.com/

21 – 22 September 2016  9th Biofuels International Conference 2016, Ghent, Belgium  
http://biofuels-news.com/conference/

18 – 20 October 2016  9th EFIB, The European Forum for Industrial Biotechnology and the Bioeconomy, Glasgow, Scotland  
http://www.efibforum.com/

2 – 3 November 2016  16th Aachener Membran Kolloquium, Aachen, Germany  
http://www.avt.rwth-aachen.de/AMK/

5 – 8 December 2016  9th IMSTEC, International Membrane Science and Technology Conference, Adelaide Convention Centre, Australia
29 – 30 December 2016
18th ICCB 2016, International Conference on Biofuels and Bioenergy, Paris, France
https://www.waset.org/conference/2016/12/paris/ICBB/home

2 – 5 July 2017
7th WHTC World Hydrogen Technologies Convention, Prague, Czech Republic
http://www.whtcprague2017.cz/
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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FLUIDCELL

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FLUIDCELL brochure