Advanced m-CHP fuel CELL system based on a novel bio-ethanol Fluidized bed membrane reformer

FluidCELL

www.fluidcell.eu

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Summary

FluidCELL aims at developing of an advanced high performance, cost effective bio-ethanol micro Combined Heat and Power cogeneration Fuel Cell system for decentralized off-grid applications.

The system will be based on:

i) design, construction and testing of an advanced bio-ethanol reformer for pure hydrogen production (3.5 Nm3/h) based on Catalytic Membrane Reactor in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit and

ii) the design and optimization of all the subcomponents for the BoP with particular attention to the optimized thermal integration and connection of the membrane reformer to the fuel cell stack.
Traditional concept

Layout of PEM m-CHP unit using traditional reforming (TR) for fuel processing

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FluidCELL concept: sweep gas layout

Layout of PEM m-CHP unit using membrane reformer (MR + sweep gas) for fuel processing
FluidCELL concept: vacuum pump layout

Layout of PEM m-CHP unit using membrane reformer (MR + vacuum pump) for fuel processing
Partnership

Multidisciplinary and complementary team: 9 top level European organisations from 6 countries: 2 research institutes, 4 universities and 3 top industries (2 SME) in different sectors (from hydrogen production to catalyst developments to boilers etc.).

1 TECNALIA, Spain
2 TU/e, Netherlands
3 CEA, France
4 POLIMI, Italy
5 UNISA, Italy
6 UPORTO, Portugal
7 ICI, Italy
8 HYG, Netherlands
9 QUANTIS, Switzerland
Consortium

1. TECNALIA, Spain
2. TU/e, Netherlands
3. CEA, France
4. POLIMI, Italy
5. UNISA, Italy
6. UPORTO, Portugal
7. ICI, Italy
8. HYG, Netherlands
9. QUANTIS, Switzerland
Project objectives

- Development of novel catalysts
- Development of high performance Pd-based membranes
- Novel catalytic membrane reactors
- Prototype reactor testing and validation
- BoP optimization
- Novel micro-CHP system
- Modelling and simulation of both reactors and complete system
- Life Cycle Analysis and safety analysis
Work Structure

WP1. Project Management (TECNALIA, all)

WP2. Industrial Specifications of Fuel CHP systems (POLIMI, ICI, HYG)
  - WP3. Novel catalytic Formulations (TU/e, UNISA)
  - WP4. Novel Membrane development (TECNALIA, TU/e)
  - WP5. Lab scale bio-ethanol catalytic membrane reformer (TECNALIA, TU/e, POLIMI, UNISA, HYG)
  - WP6. Design and Manufacturing of novel bio-ethanol catalytic membrane reformer (TU/e, POLIMI, ICI, HYG)
  - WP7. Fuel Cell Stack (CEA, POLIMI, UPORTO, ICI)
  - WP8. Integration and Proof of Concept of m-CHP system (POLIMI, ICI, HYG)

WP9. LCA and Safety analysis (ICI, HYG, QUANTIS)

WP10. Exploitation & Dissemination (HYG, all)

Modeling and Simulation (TU/e, POLIMI, HYG)
Partnership Synergies

LCA and risk assessment
- QUANTIS
- HYG
- ICI

Modelling and simulation
- TU/e
- POLIMI
- HYG

Industrial Specifications
- HYG
- ICI

Catalyst Development
- UNISAL
- TU/e

Membrane Development
- TECNALIA
- UNISAL

Lab scale Reactor
- TU/e

Prototype Reactor
- HYG

Integration and testing
- HYG
- ICI

Proof of concept
- POLIMI

Fuel Cell
- TECNALIA
- TU/e

- CEA
- UPORTO
Catalytic Materials

Objectives:

Development of a bioethanol reforming catalyst with high activity at low temperature (< 500°C) and selectivity towards hydrogen with very low formation of carbon and methane.

- The catalyst needs to be mechanically durable and operate as a fluidized bed inside a membrane reactor.
- The catalyst needs to maintain activity under membrane reactor operating conditions.
- Scale up of catalyst production
Catalyst Development by UNISA

**Mechanical support:** SiO₂ assures proper resistance during fluidization

**Catalytic support:** CeO₂ promotes dissociation of H₂O and C₂H₅OH molecules and prevents coking

**Non-noble metal:** Nickel favors C-C bond break

**Noble metal:** Platinum enhances WGS activity

**Preparation:** Sequential impregnation of CeO₂, Ni and Pt followed by drying overnight at 120°C and calcination at 600°C for 3h

**Final formulation:** 3wt%Pt-10wt%Ni/CeO₂/SiO₂
Activity tests for steam and oxidative reforming of ethanol

- **ESR**: Total C$_2$H$_5$OH conversion at 10000 h$^{-1}$ and complete O$_2$ conversion for every space velocity.

- **No effect of space velocity increase at high temperatures**
- **Reduction of conversion with contact time at T<400°C**

**Graphical representation:**
- **ESR**:
  - 10000 h$^{-1}$
  - 20000 h$^{-1}$
  - 30000 h$^{-1}$

- **OSR**:
  - Conversion plots for different space velocities.
Results of stability tests

\[ T = 500^\circ C \]

\[ \text{r.a.} = 4 \quad \text{r.o.} = 0.5 \quad \text{GHSV} = 20000 \text{ h}^{-1} \]

**ESR**

- **O**\(_2\) addition: improvement of catalyst stability 60 vs 40 h

**SEM Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Post ESR</th>
<th>Post OSR</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="C" /></td>
<td><img src="image" alt="C" /></td>
<td><img src="image" alt="C" /></td>
</tr>
</tbody>
</table>

**Thermo-gravimetric Analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon Formation Rate ( \times 10^5 ) ( (g_{\text{coke}} / g_{\text{carbon,fed}} \times g_{\text{cat}} \times \text{h}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post ESR</td>
<td>2.5</td>
</tr>
<tr>
<td>Post OSR</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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Objectives:

Development of Pd based tubular membranes, for application in bio-ethanol reforming catalytic membrane reactors

- Improved flux and selectivity
- Temperature $< 500^\circ$C
- Resistant to fluidization regime
- Process scaling up
Pd-Ag membranes by ELP

- Pd-Ag 3-4 µm thick membranes prepared by simultaneous Pd-Ag deposition on 100 nm pore size Al₂O₃ for testing at lab-scale.

- 10 membranes has been delivered
- H₂ permeance: 3.0 – 5.0 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and H₂ / N₂ >10,000 at 400 C and 1 atm (higher than the DOE 2015 target)
Ultra-thin (≈ 1 µm) supported Pd-Ag membranes by direct PVD deposition

- The Pd-Ag film is not dense on porous supports

- High selectivity H₂/N₂ can be obtained by a double process: PVD + ELP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd-Ag thickness (µm)</th>
<th>N₂ permeance x10⁻⁹ (mol m⁻² s⁻¹ Pa⁻¹) at 25 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂ 3 nm</td>
<td>~ 0.5</td>
<td>15,143±1292</td>
</tr>
<tr>
<td>PVD on ZrO₂ 3 nm</td>
<td>~ 1</td>
<td>8.5±4.8</td>
</tr>
<tr>
<td>ZrO₂ 3 nm</td>
<td>~ 1</td>
<td>24,600±434</td>
</tr>
</tbody>
</table>
Ultra-thin (∼ 1 µm) supported Pd-Ag membranes by Electroless Plating

The thickness is controlled by the plating time

The thickness is controlled by the plating time

There is a trade off between permeance and selectivity

- H₂ permeance (400°C) = 3.1x10⁻⁶ (mol m⁻² s⁻¹ Pa⁻¹); H₂/N₂ = 8,000 – 10,000
- H₂ permeance (400°C) = 4.2x10⁻⁶ (mol m⁻² s⁻¹ Pa⁻¹); H₂/N₂ = 20,000
Ultra-thin (∼1 µm) supported Pd-Ag membranes by Electroless Plating

1.3 µm thick Pd-Ag membranes: Long-term test @400 °C

After 1000 h: 
- \( H_2 \) Permeance = \( 1.0 \times 10^{-5} \) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1} \)
- \( H_2/N_2 \) selectivity = 1,900
Pd pore filled membrane

Composite nano porous membranes Packed with Palladium nanoparticles (pore filled membranes)

Advantages of pore filled over conventional membranes

- Less Pd is used (a fraction of conventional)
- Protection under fluidization regime
- Resistant to hydrogen embrittlement
Pd pore filled membrane

- Selectivity and H₂ permeance (~10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) still low.
- A second Pd pore fill coating will be added.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Membrane length (cm)</th>
<th>N₂ permeance (mol m⁻² s⁻¹ Pa⁻¹) at 25 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-A41</td>
<td>54</td>
<td>4.1 x10⁻¹⁰</td>
</tr>
<tr>
<td>PF-A44</td>
<td>55</td>
<td>4.7 x10⁻¹⁰</td>
</tr>
<tr>
<td>PF-A46</td>
<td>54</td>
<td>6.2 x10⁻¹⁰</td>
</tr>
<tr>
<td>PF-A48</td>
<td>55</td>
<td>1.0 x10⁻⁹</td>
</tr>
<tr>
<td>PF-A95</td>
<td>145</td>
<td>7.8 x10⁻⁹</td>
</tr>
</tbody>
</table>
Objectives:

- Selection of bioethanol - CMR components: catalysts, membranes and supports, and sealing based.

- Integration of these elements in lab scale reactors specifically designed for bio-ethanol reforming.

- Validation of the lab scale reactors performances and identification of the best design for prototype pilot.
Objectives:

- Design the pilot scale catalytic membrane reformer (CMR)
- Construct and assemble the pilot scale catalytic membrane reformer including controls
- Perform functionality tests before integration into Fuel Cell CHP-system
Challenges

- Fluidization regime
- Hotspots
- Adequate back-mixing
- Slugging
- Kinetic limitations
- Membrane area
- Manifolding
- Sealing

Pilot scale bio-ethanol catalytic membrane reformer
Fuel Cell Stack

Objectives:

- Selection of suitable fuel cell stack, based on the evaluation of different stack components through some single cell tests of MEA components and mainly short stack testing, both in nominal conditions.

- Definition of a PEMFC stack adapted to the m-CHP system.

- Fuel Cell stack and single cell testing to evaluate the fuel cell components in all conditions imposed by the system and hence tune the selection before some lifetime validation tests on short stacks.

- Manufacturing of the fuel cell prototype and delivery for integration into the m-CHP system. Exploitation of in-situ operation data.
Integration & Proof of Concept of CHP-System

Objectives:

- Optimization of the fuel cell CHP focusing both on technical and economic point of view (water content in bio-ethanol, membrane reactor operating conditions, membrane surface area, etc.).

- Manufacturing and testing of a PEMFC micro-CHP system.

Fuel → E (Power) → Q (Heat) → Losses
Integration & Proof of Concept of CHP-System

Activities:

➢ Definition of the reference case lay-out based on ethanol reformer and assessment of the performances.

➢ Investigation on different lay-out and operating conditions for the FLUIDCELL system.
Results:

➢ A m-CHP system model was developed. Steam reformer vs auto-thermal reformer and preferential oxidation vs methanation was investigated. The results from this analysis will be used as reference case within the project.

➢ The performance of FLUIDCELL unit is compared to the reference system composed of steam reforming and methanation, with 37% for the net electric efficiency.

➢ The layout of FLUIDCELL fuel cell CHP-system was defined. Parameters that most affect efficiency and membranes area are the water to ethanol ratio, the operative pressure of the reactor and the sweep flow rate. Net electric efficiency higher than 39% can be achieved.
Sweep gas and vacuum pump layouts comparison: effects of Water/EtOH ratio and reactor pressure on electric efficiency and Pd-membranes area.
Objectives:

- Measurement and understanding the environmental performances of the novel technology compared to the reference technology based on the LCA methodology.
- Identification of the key parameters influencing the environmental impacts, and proposal of recommendations to decrease those impacts.
- Identification and evaluation of key safety parameters on the novel technology.
- Proposal of recommendations for the safe operation of the novel technology.
Advanced m-CHP fuel CELL system based on a novel bio-ethanol Fluidized bed membrane reformer

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Thank you for your attention

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