BeingEnergy

Mid-Term Review Meeting
12th of June, 2014

RTD Coordination Aspects
Adélio Mendes, UPorfo
BeingEnergy

Integrated low temperature methanol steam reforming and high temperature polymer electrolyte membrane fuel cell.

- High temperature polymer electrolyte fuel cells operate between 160 °C-180 °C -> **Exothermic**

- Commercial methanol steam reforming catalysts show relevant hydrogen production between 240 °C-260 °C -> **Endothermic**

**Ideal situation:** couple the two reactors running at ca. 180 °C
The consortium

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<th>Partners</th>
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<td>1</td>
<td>UPORTO (Coordinator)</td>
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<td>DLR</td>
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<td>Serenergy</td>
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<td>INOVA+</td>
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<td>8</td>
<td>Rhodia</td>
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Work Packages

Integrated LT-MSR and HT-PEMFC, working at the same temperature.

WP2: Development of a new low temperature MSR catalysts
WP3: Development of a reactor for the LT-MSR;
WP4: Integration of LT-MSR with HT-PEMFC;
WP5: 350 We prototype.
Work Packages

WP2: Catalysts synthesis, characterization and modeling studies
   Leader: UPorto

WP3: Development of LT-MSR
   Leader: VTT

WP4: Integration of LT-MSR and HT-PEMFC at lab level
   Leader: DLR

WP5: Assembling and characterization of LT-MSR integrated HT-PEMFC
   Leader: Serenergy

WP6: Exploitation and Dissemination
   Leader: INOVA+

WP1: Project Management
   Leader: UPorto

RTD
Work Packages

RTD Work packages - participants

WP2: Catalysts synthesis, characterization and modeling studies

WP3: Development of LT-MSR

WP4: Integration of the LT-MSR with the HT-PEMFC – lab level

WP5: Assembling and characterization of the LT-MSR integrated HT-PEMFC

UPORTO

UPVLC-ITQ
Rhodia
Serenergy

Adélio Mendes

VTT

UPORTO
ITM-CNR
Serenergy
INOVA+

Sonja Auvinen

DLR

VTT
Serenergy
UPORTO
INOVA+

Gerhard Schuller

Serenergy

VTT
UPORTO
DLR
INOVA+

Mads Bang

New Energy World

N.ERGHY

European Union
Main targets

The proposed targets are:

**HT-PEMFC**

- Nominal electrical power: 350 We (5.6 L·min⁻¹ of hydrogen at nominal efficiency).
- Nominal electrical efficiency: > 35 % (required: 30 %).
- Lifetime expectancy: > 1500 h (required: 1000 h lifetime including 100 start-stop cycles).

**LT-MSR**

- Nominal operating temperature: 170 °C.
- Methanol conversion: > 98 % (required by the HT-PEMFC operation).
- Nominal CO concentration on the reformate: < 0.1 %.
- Lifetime expectancy: > 2000 h.

**Combined unit**

- Specific size and weight: < 35 kg·kW⁻¹ and < 50 L·kW⁻¹ (required: 35 kg·kW⁻¹ & 50 L·kW⁻¹).
- Start-up time: < 15 min.
Achievements

WP2 – Catalysts synthesis characterization and modeling studies
Milestones WP2:

✓ Pd-based catalyst (M9) – 4× more active than reference catalyst (Süd Chemie) – milestone met;

Achievements WP2:

✓ Cu-based catalyst – 1.7× more active and CO < 1000 ppm.
Achievements

Non-syngas direct steam reforming of methanol to hydrogen and carbon dioxide at low temperature

Kai Man Kerry Yu,1, Weyi Tong2, Adam West, Kevin Cheung, Tong L, George Smith, Yanglong Guo2 & Shik Chi Edman Tsang

ca. 1.4x more active @ 195 °C and 1:2 molar ratio

Figure 2 | Methanol conversion and CO content for typical steam-reforming reaction catalysts. (Reaction conditions: 0.40 g cat. + 0.40 g SC; liquid feed of CH3OH+H2O=1:2 at 0.1 ml min⁻¹; N2 carrier at 10 ml min⁻¹; 195 °C) A: 43% CuZnGaO5; B: 43% CuCeZrO5; C: 43% CuZnAlO5; D: 43% CuLaMnO5; E: 43% CuZnO2; F: 43% CuCeAlO5; G: 43% CuCeGaO5; H: 43% CuCeO2; I: 43% CuZrO2; J: 43% CuAlGaO5; K: 43% CuZrGaO5; L: 43% CuFeO5; M: 43% CuGaO2; N: 43% CuZnCeO2; O: 43% CuZnZrO2; P: 43% CuAlO2; Q: 43% CuGaZnAlO5; R: 43% CuGaCeAlO5; S: 43% CuCeZnAlO5; T: HiFUEL K120-JM commercial catalyst.
Achievements

<table>
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<tr>
<th>Sample</th>
<th>Conversion (%)</th>
<th>CO amount (ppm)</th>
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<tr>
<td></td>
<td>180 °C</td>
<td>240 °C</td>
</tr>
<tr>
<td>G66 MR-Süd Chemie</td>
<td>13</td>
<td>61</td>
</tr>
<tr>
<td>Cu_{65}Zr_{25}Al_{10}</td>
<td>23</td>
<td>100</td>
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- Cu_{65}Zr_{25}Al_{10}
Future work WP2:

- Complete the synthesis and characterization of the catalyst proposed in the DOW;

- Optimization of the industrial process for producing the new catalyst and production of the optimized catalyst;

- Optimize the Cu-based catalyst and further characterization (namely stability and activation procedure).
WP3 – Development of the low temperature methanol steam reformer
Milestones WP3:

☑️ Type of reformer (M21) – since the Cu-based catalyst is not at least 4x more active it was decided to follow with an external reformer;

☑️ Low thickness composite Pd-membrane (M24) – in progress; dense Pd-membranes were studied, other strategies proposed and under investigation.
Achievements WP3:

- Test bench description (M9) – completed;

- Reformer loaded with first catalyst (M12) – cellular and packed bed reformers developed and studied;

- Reformer simulator (M15) – simulator completed;

- Optimized reformer (M18) – reported;

- Palladium membranes (M24) – experimental and simulation work for temperatures above 200 °C reported.
Achievements

Polyphenylene sulphide bipolar plate for the cellular reformer
Future work WP3:

- Based on Serenergy design improve the reformer for low temperature using a liquid thermal fluid heat exchanger;

- Develop a CO₂ selective reactor – two approaches are being investigated: adsorption based reactor and membrane based reactor.
**Achievements**

**WP4** – Integration of the LT-MSR with the HT-PEMFC at lab level
Milestones WP4:

- Simulator predicting experimental results of combined unit (M24) – in progress;
Achievements WP4:

- Test bench (M15) – completed;

- MSR/HT-PEMFC simulator (M24) – in progress;

- Heat exchange system (M28) – in progress, liquid thermal fluid;
Achievements

Huber unit 1 (stack)  Gas feed  Control unit  Huber unit 2 (reformer)

Electric load  Stack  Space for reformer
Achievements

Stack modification prior to integration

- Application of silicone heaters on both sides of the stack to enhance time and temperature distribution during heating up
- Thermal sensors have been applied to the manifold adapters of the stack to measure stream temperatures directly at every inlet and outlet to calculate thermal energy flows

Silicone heaters

Thermal sensors
Future work WP4:

✓ In close collaboration with Serenergy develop the new energy integrated power supply using a liquid thermal fluid;

✓ Develop a CO₂ selective reactor – two approaches are being investigated: adsorption based reactor and membrane based reactor;
WP5 – Assembling and characterization of the low temperature methanol steam reformer integrated HT-PEMFC
Milestones WP5:

✓ Weight reduction (M24) – in progress: improved integrated design of the power supply, namely the use of a liquid thermal fluid;

✓ Fast start-up (M28) – in progress: a liquid thermal fluid is being introduced that will be connected to a burner for faster and more energy efficient start-up;

✓ Bipolar plates (M28) – in progress: new PPS composite were designed and tested for fuel cells and for integrating cellular and fuel cells in a single stack.
Achievements WP5:

- Test bench (M18) – completed for air cooled unit. New test bench being developed for liquid thermal fluid cooling;

- Start-up (M28) – in progress: a liquid thermal fluid is being introduced that will be connected to a burner for faster and more energy efficient start-up;

- Bipolar plates (M28) – in progress: new PPS composite were designed and tested for fuel cells and for integrating cellular and fuel cells in a single stack.
Achievements

Energy integration – View of the reformer system.
Achievements

Energy integration – View of the new liquid-cooled fuel cell stack.
Energy integration – a new approach based on a liquid thermal fluid.
Achievements

Energy integration – test of the full system.
Future work WP5:

✓ In close collaboration with DLR develop the new energy integrated power supply using a liquid thermal fluid;

✓ Complete the fast starting unit;

✓ Built and optimized energy integrated unit taking advantage of the new catalyst;
Scientific outputs
Consortium scientific outputs

✓ 8 scientific articles

✓ 1 Master Thesis

✓ Special session dedicated to BeingEnergy at ICCMR11 (Porto)

✓ EuropaCat-XI (Lyon), EFC2013 (Rome), HYCELTEC 2013 (Lisbon), ISGC2 Congress (La Rochelle), 64th Annual Meeting of the International Society of Electrochemistry (Santiago de Queretaro, Mexico) and World Hydrogen Conference (China).
General Conclusions
General conclusions:

- Commercially, only low cost catalysts should be developed;

- The best Cu-based catalyst developed is more active than the best described one, it is ca. 1.7x more active ($W/F^0 = 30 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{s}$) and produces less than 1000 ppm of CO at the working conditions;

- The new catalyst is not enough active for a cellular reformer/fuel cell stack approach;

- Strategies for improving the effective reaction kinetics at high conversions based on the selective removal of $\text{CO}_2$ from the reaction medium are being pursued, namely:
  - Adsorption reactor;
  - Ionic liquid absorbent/membrane based reactor.
General conclusions:

- A new energy design is being developed based on a liquid thermal fluid;

- A new starting up design allows much faster start-up;

- HT-PEMFC life time longer than 8000 h (required 1000 h and proposed 1500 h);

Proposed new reference values are:

- Reforming and fuel cell operating temperatures – 180 °C;

- Nominal power supply power – 500 We.
Thank You

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