

PROJECT PERIODIC REPORT

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Project acronym: METPROCELL

Project title: Innovative fabrication routes and materials for **METal** and anode supported **PROton** conducting fuel **CELLs**

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Publishable summary

A.- Description of METPROCELL project

Proton Conducting Fuel Cells (PCFCs) represent one of the most promising technologies to reach the requirements related to cogeneration application, especially for small power systems (1-5 kWe). This technology shares the thermal and kinetic advantages of intermediated temperature operation at 500-700°C with molten carbonate and solid oxide fuel cells, and the intrinsic benefits of a proton diffusion observed at low operating temperature in proton exchange fuel cell (PEMFC/PAFC). Within this intermediate temperature range (specifically 400-600°C), non-precious metal catalysts and oxide-type catalyst supports and electrode materials can be used, while the problem of thermal ageing of SOFC components is avoided to some extent.

The implementation of PCFCs could significantly contribute to industrialise the fuel cell technology by improving the cell characteristics (thermal cycling, heat transfer, current collection..) as well as lowering drastically the costs of the whole system (use common metal materials). This challenging task can only be achieved with interdisciplinary research between R&D institutions and industry, covering all the aspect of the chain, from materials (electrolytes, electrodes and supports) to cell/stack design, system engineering and related environmental issues. All these fields are covered by the METPROCELL project.

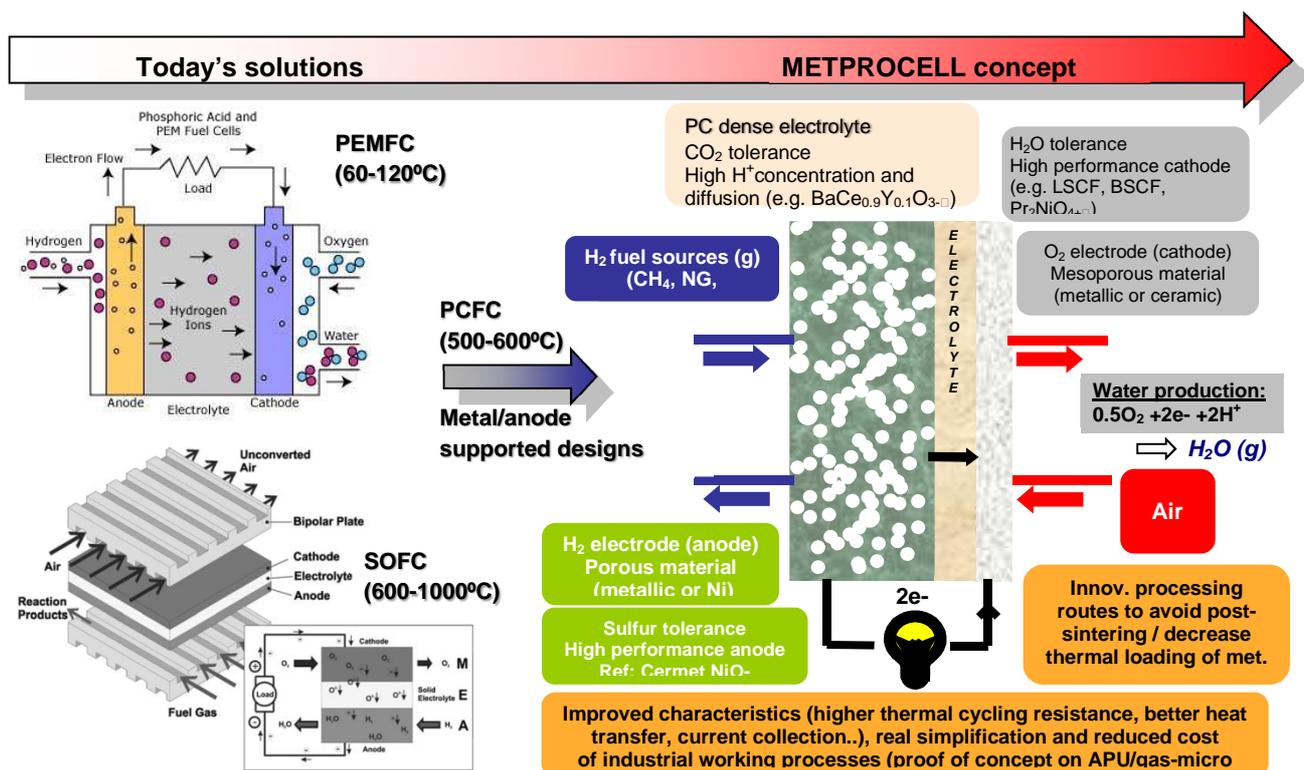


Figure 1: METPROCELL project concept.

The aim of METPROCELL was to develop innovative Proton Conducting Fuel Cells (PCFCs) by using new electrolytes and electrode materials and implementing conventional as well as new alternative fabrication routes. Following a complementary approach, the cell architecture shall be optimised on both metal and anode type supports, with the aim of improving the performance, durability and cost effectiveness of the cells. Moreover, METPROCELL aimed to bring the proof of concept of these novel PCFCs by the set-up and validation of prototype like stacks in relevant industrial conditions.

The scientific and technical objectives to achieve this general objective were the following:

- To understand the fundamental mechanisms (i.e; oxygen reduction reaction at the cathode side, structure-property-performance and manufacturing process relationships) in order to obtain electrodes and electrolyte materials with radically enhanced properties.
- To gain a deeper understanding in how to shape electrodes and electrolytes for PCFCs using conventional wet chemical methods.
- To gain a deeper understanding in how to deposit the different cell components by thermal spraying for the manufacture of next generation fuel cells with focus on both: 1) Processing of fine structured ceramics by thermal spraying in order to obtain thin and gas tight ceramic layers for application as electrolytes and protective coatings; 2) processing on novel material formulations to produce porous electrodes layers.
- To investigate innovative metal and anode support architectures with enhanced performance and long term stability with the aim of obtaining the next generation of proton conducting fuel cells.
- To assess the long term stability (target>500h) of the developed PC cells under relevant service conditions for both lab-scale samples and up-scaled stack cells, with special focus on the characterization of the related degradation mechanisms.
- To achieve more than 400 mW/cm², 0.6V at 600°C for PCFC cells.
- To assess PCFC technology as electrolyser.
- To manufacture and test the first complete PCFC 5-cells stack unit.

For a maximum impact on the European industry this research, covering the complete value chain of the PCFC stack manufacturing, could only be carried out with a multidisciplinary and complementary team having the right expertise, including top level European Research Institutes and Universities (4 RES) working together with representative top industries in different sectors (from raw materials to fuel cell technology suppliers) (2 SME and 2 IND).

The **METPROCELL** Project has been funded under the European Community's Seventh Framework Programme for the Fuel Cells and Hydrogen Joint Technology Initiative. The Project has started the 1st of December of 2011 and lasted for 42 months.

B.-Description of the work performed since the beginning of the project

- The first step of the project consisted of the collection of industrial specifications, selection of the most promising materials and definition of standard test protocols for the in-situ electrochemical testing of button (single cell level) and large stack cells (stack level).
- Development of new materials for PCFCs:
 - *Electrolytes:* Additions of NiO / ZnO are efficient to fully densified BCY and BCZY at 1200°C. No changes conduction in mechanism. ZnO BCZY (7mS.cm⁻¹) showed to be more conductive than BCZY. Moreover, a novel electrolyte composition BCZYYb-ZnO with a σ_{H^+} value as high as 14 mS.cm⁻¹ was obtained.
 - *Anodes:* (1) Ni-BCZY cermets elaborated at 1450°C with conductivity > 1000 S.cm⁻¹ at 600°C. (2) Ni-BCZY elaborated at 1200°C showed higher porosities. Ni-BCZY/BCZY-ZnO/Ni-BCZY cells (co-pressing / co-sintering) led to dense / crack free electrolytes and very good cermet/electrolyte interfaces. The ASR is strongly dependent on the p_{H₂}. At 600°C in a 97% H₂ / 3% H₂O, the ASR is extremely low: 0.07 Ω.cm².
 - *Cathodes:* Four selected MIEC (O²⁻/e⁻) oxides investigated: 2 cubic perovskites La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} (LSCF) and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) and the Ruddlesden-Popper nickelate, Pr₂NiO_{4+δ} (PrN) with the K₂NiF₄-type structure. The water insertion in these materials has been discussed on the basis of thermo-gravimetric analyses, giving a first indication of a possible protonic conduction in these oxides. Cathode layers (Pr₂NiO₄ and BSCF) showed under air with high p_{H₂O}, σ values ≥ 50 S.cm⁻¹ at 600 °C. The ASR values < 1.0 Ω.cm² have been measured for single phase electrodes at 600 °C. Additionally, architected BSCF/BCZY cathodes with ASR down to 0.44 ohm.cm² have been developed;

with novel compositions tested during the third year of activities (SmBSCF-BCZY) featuring higher chemical stability and electrochemical performance.

- Development of anode supports: Half cells have been elaborated using the previously developed anode materials with the required conductivity, porosity and electrochemical properties. Additionally, a bi-layered Ni-BCY anode support has been developed.
- Development of metal supports: Low cost ferritic stainless steels (Iron Chromium steels) porous supports with Thermal Expansion Coefficients (TEC) close to that of the electrolytes ($10 \cdot 10^{-6} \text{ K}^{-1}$) and porosities around 44% (far over the requirement of >30%) have been manufactured. The corrosion resistant of these supports have been characterized under relevant service conditions (humid H_2 at 600°C for 1000 hours of operation). In order to improve the corrosion performance of the supports, different attempts have been done to develop Ce or Y based protective thin films. Flat supports with a size of 100 x 100 mm have been manufactured for the development of cells by both conventional wet routes and alternative procedures via thermal spray techniques.
- Development of cells by wet chemical routes: Both anode supported and metal supported cell architectures have been investigated. (1) Anode supported cells: Tapes of BCY-NiO and BCZY-NiO with (450 μm thick) were successfully casted. BCY/BCZY/BCYZ-ZnO electrolyte layers (5-10 μm thick) deposited by screen-printing and a co-fired to flat half-cells (3.5 x 3.5 cm^2 after sintering). Electrolyte deposition by spray coating has been investigated as an alternative method to co-pressing to get thinner (<20 μm) and more homogeneous electrolytes (additional compositions were tested with this method: BCZYYb-ZnO). (2) Metal supported cells: Main difficulty associated with oxidation of the metal. Most promising sintering atmosphere consists of 5% H_2 (or more) in pure Argon (N_2 should be avoided as sintering gas because of the formation of chromium nitride). Promising results were obtained, but it was concluded at the project midterm that significant research efforts are still needed to obtain well structure cell components using this route. Activities were stopped and efforts were focused on the development of anode supported cells.
- Investigation of alternative cell manufacturing procedures:
 - *Plasma Electrochemical Vapor Deposition (EVD):* Thin BCY electrolytes on porous metal supports deposited with and without anode layer showed that the high surface roughness and porosity of the support (around 20%) remains the main bottleneck for the elaboration of uniform half-cells. The implementation of a graded support structure seems to be mandatory. Results collected until the project midterm led to the conclusion that significant effort are still required to fully assess the potential of this method.
 - *Thermal spraying:* (1) BCY-NiO and BCZY-NiO anode layers developed by APS. Best electrochemical performance obtained with cermet feedstock powders, with homogenous distribution of phases at the sub-micro scale with ASR values down to 0.45 $\Omega \cdot \text{cm}^2$. As an alternative processing route, a proprietary High Velocity Oxygen/Air Fuel (HVO/AF) process from TECNALIA was investigated, leading to NiO-BCYZ-ZnO anode layers with a clear pore network after the reduction treatment and moderate electronic conductivities. An additional benefit gained with this HVO/AF technique is the improved adhesion to the metal support, which results from the much higher kinetic energy reached by the powder particles in comparison to APS. (2) Assessment of different atmospheric thermal spray technologies for the development of BCY/BCZY-ZnO electrolytes with the required gas tightness: Electrolytes with thickness down to 25-40 μm and a large retention of the initial crystallographic structure have been obtained by HVOF spraying, but gas tightness seems only to be possible after an adequate thermal treatment. (3) BSCF / Pr_2NiO_4 cathode layers with moderate porosity and large retention of the initial crystallographic structure by APS (electrochemical performance under the threshold).
- Corrosion testing of candidate alloys for the development of interconnect plates under relevant service conditions for PCFCs. Based on decision taken by the 1st project review, the development of protective layers on interconnect plates was stopped in the project midterm.
- In-situ electrochemical testing of button cells: Different anode and metal supported cell configurations have been manufactured for in-situ testing, thus employing half cells based on both reference BCY and advanced BCZY(Yb)-ZnO electrolyte compositions. Optimized architected screen printed cathodes have been used for all selected configurations. For the

hydrogen electrode supported configuration, single PCFCs with a max. power density of 513 mW.cm⁻² at 600°C have been obtained. Max. power density achieved so far with the developed metal supported cell configuration is limited to 43 mW.cm⁻² at 650°C. In the last case, further RTD activities are still needed to optimize the processing route and decrease the functional thickness of the electrolyte.

➤ Up-scaling of manufacturing procedures:

- Manufacturing routes for all reference electrode and electrolyte powder materials have been up scaled and can be produced at industrial scale by the involved SMEs with the expected phase purity and particle size distribution.
- *Manufacture of cell components for anode supported cells:* The anode-supported design remains the most mature technology for the manufacture of stack cells. The up-scalability of selected cell configurations to a foot print of 120 x 120 mm² has been assessed under lab conditions. Different generations of supports were manufactured in the way of improving the Ni percolation. Even if an improved Ni percolation and thus electronic conductivity could be demonstrated, the performance of the supports manufactured by the industrial partner in charge during the co-sintering step (anode + electrolyte) remained a bottle neck for the achievement of flat and high quality half-cells. After first unsuccessful attempts to reproduce the anode support quality achieved at lab scale, parallel strategies have been implemented for the up-scaling of different cell configurations as back-up solutions. Few anode supports in size of 120 x 120 mm² with the required quality could be delivered. Full cells in size of up to 70 x 70 mm² could be produced at lab-scale by tape casting (support) and screen printing/wet powder spraying (electrolyte/air electrode).
- *Manufacture of cell components for metal supported cells:* (1) Metal supports: Flat supports with symmetric porous structure and enhanced corrosion resistance are available for cell manufacturing in size of up to 100 x 100 cm. (2) Wet chemical routes: Different attempts have been done to optimize the co-sintering treatment of the half-cell (metal support / anode / electrolyte), but the high surface roughness of the supports and need to further optimize co-sintering treatment (match the shrinkage of the electrolyte and the support) are still the limiting factors to obtain thin layered and well-structured cell components. (3) Thermal spraying route: Developed hydrogen electrode layers can be produced on large supports by either plasma (APS) or HVOF/HVAF spraying with high reproducibility. The same apply for the developed electrolyte layers. The challenge is to meet the industrial dimensional requirements (overall cell thickness by 325 ± 25 μm) is linked to the deformation of the support during electrolyte deposition by either detonation or HVOF spraying, imposing the need to employ metal supports with thickness over 600 microns.

- Performance validation of up-scaled cells: Due to the difficulty in upscaling the cells, the electrochemical testing of up-scaled cells was limited to disc shaped cells with 60 mm in diameter. Performances are in the same range than those measured on lab-scale cells, which validates the up-scaling process for the manufacture of large samples. Different kinds of profiles (micro-cogeneration, reversibility) have been applied to simulate various operating conditions. Low degradation rates have been calculated under fuel cell mode (no degradation under constant polarization, -1.5%/kh), whereas further improvements have to be done for the electrolysis mode.

C.- Final results and their potential impact and use

The **METPROCELL** project structure is broken down following the focus on material development for novel electrolytes, electrodes and supports as well as on processing methods for the deposition of thin layered cell components and shaping of functionally graded supports. The main results collected in the project are:

1) Novel electrolyte and electrode materials and up-scaled manufacturing procedure of the same, leading to a new generation of electrolytes more tolerant to CO₂ and dedicated to 500-600°C:

- BSCF/BCZY cathodes with ASR down to 0.44 ohm.cm²; SmBSCF-BCZY / cathodes with higher chemical stability and electrochemical performance.

- BCZY-NiO anodes with ASR down to 0.07ohm.cm^2 and $\sigma_e > 1000 \text{ S.cm}^{-1}$
- BCZYYb-ZnO electrolytes with σ_{H^+} of 14 mS.cm^{-1} .

2) Anode supported button cells (Conf. Ni-BCZY / BCZY-ZnO / SmBSCF-BCZYYb / SmBSCF) with very high maximum power densities of 513, 630 and 762 mW.cm^{-2} at 600, 650 and 700°C, respectively [using air as the oxidant gas and humid H₂ (3%vol. H₂O) as fuel gas - cell geometry: 30x30 mm].

3) Low cost ferritic stainless steels (Iron Chromium steels) flat porous supports with Thermal Expansion Coefficients close to that of the electrolytes ($10 \cdot 10^{-6} \text{ K}^{-1}$) and improved corrosion resistance under humid H₂ at 600°C (oxide thickness below 1 μm after 1000 hours of operation) thanks to Ce or Y based coating (with porosities around 44% porosity, far over the requirement of >30%). Facilities for large scale production are available within the consortium.

4) Cell up-scaling: Up-scaled anode supports with metallic behaviour and good percolation of the nickel phase, $\sigma_e = 1280 \text{ S.cm}^{-1}$ at 600°C, crack-free 600 μm thick (some improvements are still required to meet the target size of 120 x 120 mm^2 with sufficient reproducibility). Selected cell configurations up-scaled to 70 x 70 mm^2 and tested under relevant service conditions at lab-scale. Durability & Micro-cogeneration profile tests led to the following results: Durability: $\delta V/V = +3.6\%/1000\text{h}$; micro-cogeneration (dynamic) profile: $\delta V/V = -1.5\%/1000\text{h}$. SSC and SmBSCF materials as air electrode components seem to be more efficient than BSCF one, as very high power densities have been measured (more than 0.5 W/cm^2 at 600°C). METPROCELL' results are among the best results published in the literature.

4) For the first time, the PCFC technology has been assessed at lab scale level in electrolysis mode (900 mA.cm^{-2} at 1.3 V and 700°C - Stability: 7%/kh). Lower ASR in EC mode compared to FC mode.

Based on preliminary cost assessments, the actual performance and maturity level of SOC technology allows itself to be more competitive in terms of manufacturing cost than those obtained with PCC technology towards operating temperature around 700°C (around factor 1.7). However, the expected improvement of electrical performance and reliability of PCC at 700°C could drastically reduce such gap (values around **1.8 €/W** are predicted).

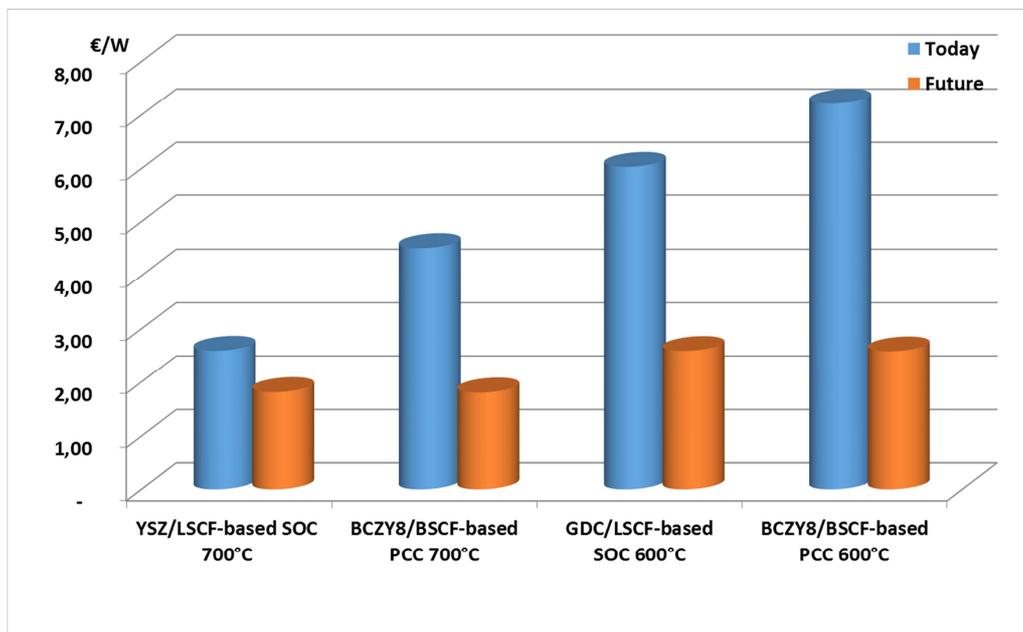


Figure 2: SOC and PCC manufacturing costs under fuel cell operation.

At 600°C, SOC and PCC are now under deep investigations to elaborate a reliable and high performing cell. Thereby, the difference between the two technologies is limited and estimated values could easily cross over around **2.6 €/W**.

The electrolysis profile could be more profitable than fuel cell mode for PCC technology. Even though under equivalent conditions the cost of produced hydrogen at 700°C using actual PCC is estimated to be higher (around 19 €/kg_{H2}) than the cost using actual SOC (around 14.3 €/kg_{H2}), the expected electrical performances for both PCC & SOC technologies in the near future would allow a strict reduction of the gap price between the two technologies to around 4.6 €/kg_{H2} @700°C. Even more, PCC could benefit to a high interest below 700°C caused by both the lack of competition with SOC (no data revealed until now in the literature) and an expected significant reduction of electrical degradation with time, by considering the smoother operating conditions (lower temperature). The actual electrical performances of PCC obtained at 600°C in the frame of METPROCELL at industrial scale doesn't permit to get a competitive cost of produced hydrogen (19 €/kg_{H2}). However, it can be noticed that such value is lower than those obtained at 700°C thanks to a lower depreciation of system with time (hyp: 20 000h) at lower temperature. Additionally, by considering potential electrical performances already validated in the frame of the project at lab scale, the price of hydrogen produced could be competitive with SOC technology operating even at higher temperature (4.6 €/kg_{H2} @600°C).

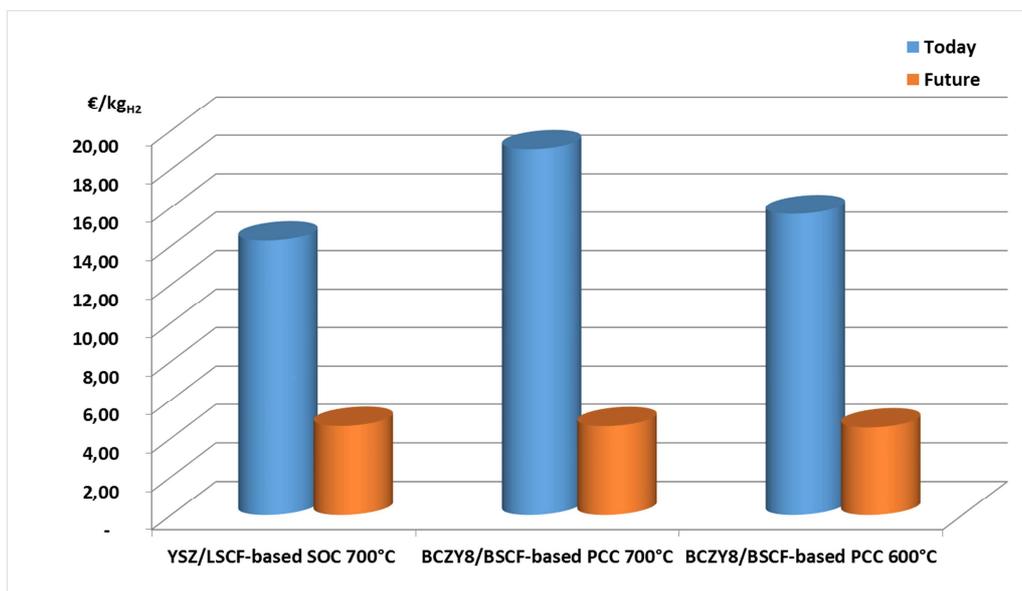


Figure 3: a) SOC and PCC manufacturing costs for electrolysis operation (in €/W) and b) the tentative cost of hydrogen produced (in €/kg)¹.

Finally, for the developed metal supported PCFC (anode/electrolyte deposited by thermal spraying + cathode by screen printing), an electrical performance of 0.3 W/cm² would be sufficient to target a competitive cell cost of 2.5 €/W vs. anode supported cell configuration (current performance: 43 mW.cm⁻² at 600°C). A potential reduction to 1.7 €/W for large scale production could be expected.

The PCFC technology could significantly contribute to industrialise the fuel cell technology by improving the cell characteristics (thermal cycling, heat transfer, current collection..) and lowering drastically the system costs. Following impacts are expected:

- The possibility to reduce the service temperature under 600 °C will be notably useful to prolong the service life of the metal supports potentially beyond current benchmarks of 40.000 hours.
- The new PCFCs may offer some further advantages for the environment such as higher fuel utilisation in comparison to the SOFC technology.

¹ Hypotheses retained: [Fuel utilization = 50%] [electrical efficiency: 90%] [cell lifetime: 20 000h], [$\delta V/V_{600^\circ C}=1.5$ %/kh actual and 0.5%/kh expected, $\delta V/V_{700^\circ C}=$ actual 2 %/kh and expected 1.5%/kh] [Cost of electricity: 60€/MWh, PCI = 33.33 kWh/kgH₂] [Margin profit = 20%].

- Increase of system efficiency, through a better utilization of the heat produced and a smaller BoP, a lower operating temperatures down to 600 °C, a reduction of the energy consumption of at least 7- 10% and the elimination of the fuel dilution (since water is formed at the cathode).

D.- The address of the project public website

www.metprocell.eu/