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4.1 Final publishable summary report

IDEAL-Cell project

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A - Executive summary

Concept

The IDEAL-Cell project aimed at fabricating an innovative fuel cell concept based on a dual membrane with mixed protonic and anionic conduction and operating at 600-700 °C. This new system, combining the benefits of PCFCs and SOFCs while evading their disadvantages, consists in assembling the anode/electrolyte couple of a PCFC and the cathode/electrolyte couple of a SOFC through a porous central membrane (CM) wherein water is formed (figure 1), and from which the water is evacuated. Therefore, in IDEAL-Cell, hydrogen, oxygen and water are located in **3 independent chambers**, which allows avoiding all the detrimental consequences linked to the presence of water at electrodes (low fuel and electrical efficiency, interconnect corrosion, need for a gas counter-flow...) that are found in standard SOFCs and PCFCs.

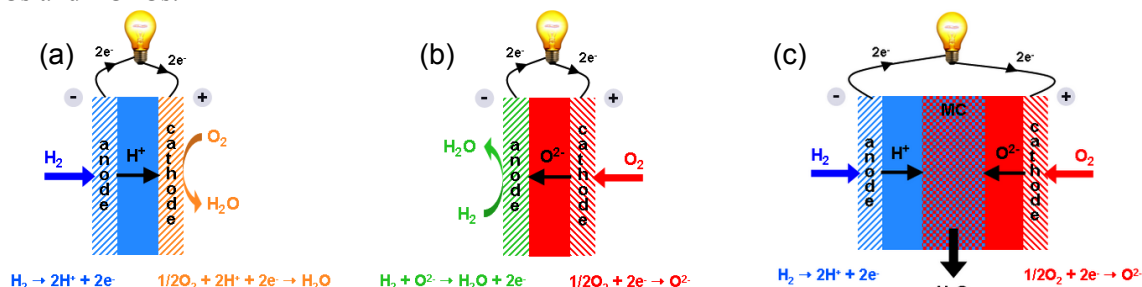


Figure 1. Schematic of (a) a PCFC, (b) a SOFC and (c) the IDEAL-Cell concept.

The project was divided in two phases, the first one (2 years) dedicated to the proof of the concept, the second phase (2 years) to the fabrication and optimization of single dual cells.

Phase I: Proof of Concept

The validity of the IDEAL-Cell concept has been experimentally proven after two years of intensive shaping, modelling and electrochemical testing. To prove the concept, four criteria were verified: (i) stable value of the OCV, (ii) stable V/I polarization curve, (iii) specific complex impedance fingerprint associated with the formation of water, and (iv) clear, direct and quantitative evidence of water formation within the CM. Electrochemical tests were performed on dedicated proof of concept (PoC) testers and samples. Such PoC test was operated in front of EC experts during the mid-term review of the project (Genoa, March 23rd, 2010. The experts acknowledged the validity of the proof of concept demonstration.

Phase II: Fabrication, optimization, integration of dual cells in a short stack

Following the EC recommendations, the objectives of Phase II were slightly re-orientated towards a deeper understanding of the elementary mechanisms at stake and improvement of performances. An electrochemical theoretical description of IDEAL-Cell has been developed: it shows that a drastic decrease of the electrodes overpotentials could be expected, and that losses were almost totally restricted to the CM. The theoretical model, along with sophisticated 3D microtomography experiments and mathematical morphology reconstruction, was used to guide the cell shaping. Full IDEAL-cells were then obtained via either an optimized sequence of standard shaping processes (tape casting, screen printing, wet powder spraying, cold pressing) or by plasma spraying. This has allowed fast increasing performances to take place within months, (1 mW/cm² in early 2010, up to more than 100 mW/cm² in late 2011 for still thick samples). Experimental comparison of IDEAL-Cell with SOFC and PCFC with comparable geometries (size, thickness) obtained via the same processes, along with theoretical extrapolation toward lower thicknesses, showed that IDEAL-Cell has better performances than that of SOFCs and PCFCs, but with none of their drawbacks. IDEAL-Cell was proved to be very flexible in terms of operating temperature, the optimum being between 600 °C and 700 °C, and is fully reversible (fuel cell versus electrolyzer mode), thanks to its high symmetrical geometry. In the electrolyzer mode, O₂ and H₂ are produced in 2 separate chambers, and a new mechanism of conduction based on the formation of a nanometer thick ordered layer of water at the internal surface of the CM was discovered.

B - A summary description of project context and objectives*Context*

Because of their potential high efficiency, high temperature fuel cells (SOFCs and PCFCs) are promising systems to co-generate electricity and heat for stationary applications. The most achieved high temperature fuel cells are the so-called SOFCs, and very few companies have brought them to a pre-commercialization segment, mainly as large stationary systems in North America, combining heat and power generation, and as power plant and residential systems in Europe. Asian countries begin to be incredibly active in that field, and more and more presentations at international congresses show technical realization that seem close to the market. Though more expensive (\$1000-1500/kW) and less efficient than planar SOFCs (\$600-800/kW), the tubular SOFC systems are more mature in their development. Diverse variations do exist between these two geometries; manufacturers giving their own twist (*i.e.* Sulzer design, the High Power Density elliptical design by Siemens-Westinghouse, the Rolls-Royce design...). In either case, these systems are operated in the range 800 °C-1000 °C, and are based on Yttria-Stabilized Zirconia (YSZ) as the electrolyte material. The anode is usually a Ni-YSZ cermet, whereas the cathode is generally a lanthanum-strontium manganese oxide (LSM).

Since there are many technical drawbacks in operating a SOFC at such a high temperature (glass ceramic seals, exotic interconnects, components failure and ageing, long time to heat-up and cool-down to avoid thermal shocks...), there have been recent developments to bring the operating temperatures of SOFCs down to the 500-600 °C range, through the concept of anode supported design, on which a thin layer of electrolyte is deposited (low resistance, but increase of the cathode/electrolyte polarization) and through materials development (SOFC based on GDC and LSC). Another approach concerns the venue of a different mechanism for conduction (proton conducting ceramic based fuel cells –PCFC). Lots of improvements have been made by a large number of researchers on these two concepts, in particular in the USA, in Japan, in Switzerland and in a certain number of European countries. Though not yet really commercialized on a routine base, fully operational SOFC short stacks based on GDC operated in the range of 600-650 °C are already available. As an example, Ceres Power Ltd has recently developed a GDC based SOFC operated at 500-600 °C based with encouraging levels of durability and tolerance to thermal cycling.

Programs on the development of PCFC short stacks are being under way in a few countries, and some prototypes have been proposed by start-ups; at the same moment, efforts are made at national level in a few countries in order to give an impetus to this appealing concept. But PCFCs are much less developed than SOFCs, and need some more extensive research efforts, in particular to enhance the stability of the electrolyte, to fully understand the proton hopping process on oxygen sites in the electrolyte material, to develop an appropriate cathode material and to design a low cost interconnect for the cathode side that is resistant to oxidation by high temperature oxygenized water.

Nevertheless, though potentially very attractive on the long term, even the more mature SOFC systems based on YSZ show efficiency hardly higher than 40 % for the hydrogen consumption (up to 80 % if recycling with gas counter-flow), and an electrical efficiency in the range of the 50 to 60 %. This, in addition to the important costs of development and manufacture, strongly slows down their marketing. The basic reason for this lack of efficiency is that the standard design of either SOFC or PCFC is flawed since the very beginning, in the sense that fuel is diluted by water at the anode in SOFC, and water is present on the cathode side in PCFC. Consequently, in addition to the decrease of the fuel efficiency, this exerts a very high constraint on the design and on the materials for both SOFC and PCFC electrodes as well as on the interconnect architecture and materials.

On the SOFC anode side, the system must be "open" so that a flow of gas can be generated in order to evacuate the water vapour, and the microstructure as well as the materials cannot be fully optimized for its basic purpose, that is the recombination of incoming oxygen ions with dissociated hydrogen molecules

with the release of electrons towards the external circuit. On the cathode side of a PCFC, the interconnect and the cathode materials have to deal with a highly corrosive mixture of oxygen and water at high temperature. Though less impeding than for the SOFC anode, the presence of water strongly decreases the electrical efficiency of the PCFC cathode. This PCFC cathode compartment must also be left "open" so that water can be evacuated. The systematic necessity of a counter-flow to sweep water out of the catalytic sites is also energy consuming, in addition to the fact that it also acts against the preliminary heating of the fuel. For different reasons, all linked to the fact that water dilutes either hydrogen in SOFC or oxygen in PCFC, co-generation of electricity and heat –though theoretically very attractive– remains difficult: on the one hand in SOFC water vapour can carry heat out of the system, but along with a large amount of fuel, which efficiency decreases accordingly; on the other hand, in PCFC water vapour carries heat out of the system, but along with oxygen, leading to a mixture that is highly corrosive for the interconnect material, which must be coated with a protective layer to resist this severe corrosive attack.

In view of all the arguments developed above, we have reached the conclusion that a high temperature fuel cell design that could isolate the hydrogen compartment and the oxygen compartment from the exhaust water could bring a real innovative impetus to the development of high temperature fuel cell. This would allow to solve all the problems associated with the presence of water on the SOFC anode side and PCFC cathode side (dilution of fuel, corrosion by high temperature oxygenized water, condensation of water on the catalytic sites, no gas flow to sweep the water out...); in such a design, each compartment has a single role to play, and as such can be fully optimized, and can be operated independently via the appliance of a pressure to enhance the overall efficiency.

Since both SOFC and PCFC technologies are available in their principles, though not at the same degree of maturity, and the corresponding materials are made routinely, and considering that exactly the same basic chemical equation is used for both systems (hydrogen + oxygen $\rightarrow$ water) and that the production of water is rejected towards the anode side for SOFCs and towards the cathode side for PCFCs, the consortium came to the very simple idea that a **three independent compartments system** could be developed by joining the cathode part of a SOFC to the anode part of a PCFC; in such a design both parts reject the production of water towards a common central compartment. Therefore, protons are created at the PCFC anode side from hydrogen rich gas, then diffuse through the PCFC electrolyte towards the central membrane; oxygen ions are created at the SOFC cathode side, diffuse through the SOFC electrolyte towards the central membrane. Protons and oxygen ions combine in the central membrane, with only the need for a local transfer of electrons. Therefore, the electrons that are torn off atomic hydrogen at the PCFC anode go to the external circuit to feed atomic oxygen to create oxygen ions at the SOFC cathode side. The central membrane, which is the core of the project, must be a mixed proton and oxygen conductor, and must be highly porous to allow the evacuation of water. As the electrode is a mixture of three percolating conducting media (for ions, electrons and gas), the three conducting networks in the IDEAL concept central membrane (proton conductor, oxygen conductor and gas conductor) must percolate. The production of water is therefore totally independent of both electrodes of the system.

In such a design where the three chambers (H, O and water) are independent, it became evident that **each chamber could be "fine-tuned" for an exclusive purpose** in terms of catalytic activities, gas pressure, water evacuation, without compromising to take into account the gas dilution, condensation of water on the catalytic sites, inhibition of mass transfer, corrosion by oxygenized water at high temperature. In addition, like in an internal combustion engine, this concept allows easily applying a pressure independently on both H and O electrodes to tailor and enhance the efficiency of the system, which is impossible –or extremely difficult– in standard SOFCs and PCFCs.

The first and immediate requirement for such a system is that an operating temperature acceptable either for the oxygen side or for the hydrogen side is to be found. A major concern lies in the fact that SOFCs and PCFCs are not intended to operate at the same temperature (respectively 700 °C-900 °C for SOFCs, and 500-600 °C for PCFCs). Nevertheless, Ceria based SOFCs are routinely operated at 500-650 °C, and our own results on a typical PCFC electrolyte (BCY10) at 600 °C are very encouraging ($\sigma = 2.10^{-2}$ S/cm). Therefore, the concept arose in a highly favourable situation where all the materials were available on a

routine basis, with potentially very good properties in the range 600-700 °C. This is the targeted range of operating temperature for our dual cell.

Objectives

The present project clearly intended to bring significant innovations to the field of the high temperature fuel cell technology for stationary applications; these innovations can be drawn from our new concept of a high temperature fuel cell system with three independent compartments. To that purpose, the final objective of the project was the ***fabrication of a dual cell short-stack, with optimized properties and operating conditions, operated in the range of 600-700 °C under hydrogen, via low cost forming processes***. The short-stack should have consisted of two dual cells integrated in a interconnect architecture designed specifically to take advantage of the concept of three independent chambers. As mentioned in the executive summary, the project has been re-oriented slightly after the mid-term review recommendations, and the realization of a short stack was not anymore the focus of the project, even if a specific stack design for housing IDEAL-Cell has been studied. Having in view a drastic enhancement of the efficiency of high temperature fuel cell systems (fuel efficiency, electrical efficiency), on the long range the project aimed at reducing the GHG emission. Beyond the scope of the present objectives, this system is thought to be easily coupled to a simplified heat-exchange system (via high temperature water non diluted with a fuel), to a vapour-reforming system (production of ultra-pure water that does not need any purification stage) and to be reversible (operating either as a fuel cell or as an electrolyser, reversibility which has been effectively proved during the project).

To fulfil the ambitious objective presented above, the project proceeded in successive steps of reasoned difficulties; the first phase (2 years) was dedicated to the proof of the concept, and to the development of a dual cell using existing materials, by successively approaching the manufacture of the anodic compartment and the cathodic compartment, then of the central membrane. The second phase (2 years) was dedicated to the optimization of the central membrane and the cell through the development of specific materials and numerical modelling.

In proposing a new concept in the field of high temperature fuel cell with numerous advantages compared to existing technologies, the present project clearly corresponds to the topics addressed by the call (*topic ENERGY.2007.1.1.3: innovative concepts for fuel cells, innovative design for fuel cell stacks, development of related new materials and processes, which can lead to breakthrough concepts with potential for substantial improvement in fuel cell performance, durability and cost reduction...*).

The development of this innovative IDEAL-Cell concept required tackling scientific and technical key-issues (that are precisely and extensively described in the DoW), in the field of electrochemistry, solid state chemistry, thermodynamics, diffusion, sintering, chemistry, chemical engineering, metallurgy, ceramics, corrosion, ceramic processing, analytical characterization, fluid dynamics, finite elements, mathematical morphology, impedance spectroscopy, engineering, mechanics, electrical engineering, scaling-up and benchmarking, management. Research includes theory and extensive modelling in some of the above scientific fields. The consortium was precisely chosen so that it presented all the required expertises in a complementary way, expertises that are recognized nationally (involvement in national programmes) and internationally (international partnership with prestigious institutions in the field, international programmes). The consortium was also recognized at the European level (the European Science Foundation awarded a proposal for an Exploratory Workshop involving the consortium on Proton Conducting Materials For Next-Generation of Solid Oxide Fuel Cells which was organized by partner 3 – CNR– in 2007).

C - Description of the main S&T results/foregrounds

The following text will present on the one hand the detailed scientific and technical results year by year and workpackage by workpackage, and on the other hand a focus will be made on what have been the major highlights of the project.

Detailed year by year technical advances and results

The technical approach was a systematic 1 by 1 step approach that tackled first the cathode compartment (WP2), then the anode compartment (WP3), then the dual central membrane (WP4) to reach the proof of concept validation after 2 years. When the concept was validated, and following the EC recommendations suggested at the mid-term review, the consortium strengthened the basic knowledge on each compartment in view of a better understanding of the basic mechanisms, improvement of materials, components and cell, with a strong focus on the dual conducting central membrane (WP5, see figure 1). The following sections will describe for each yearly period (year 1 to year 4) the scientific and technical advances and results workpackage by workpackage.

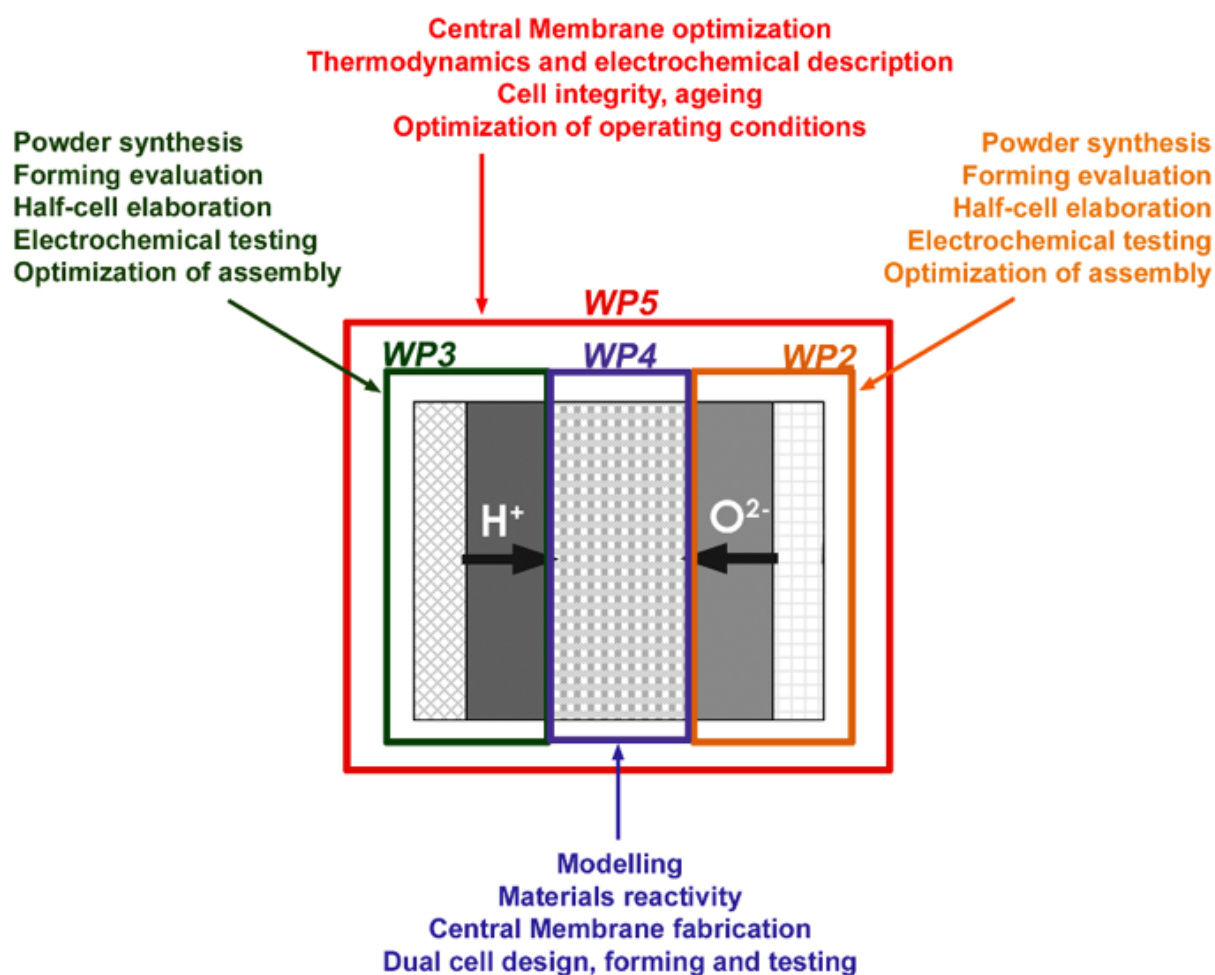


Figure 1. Technical workpackages and organization of the project

Year 1

In the first part of the project (Phase I), the essential goal consisted in proving the IDEAL-Cell concept. For that purpose, in the first year the consortium principally focused its technical and modelling activities in WP2 (Oxygen Electrode Assembly Development), WP3 (Proton Electrode Assembly Development)

and WP4 (Dual Cell Realization). WP4 was obviously the critical workpackage for the GO/NO decision in the sense that it was dedicated to the core of the concept, that is the mixed conducting and porous central membrane. In addition, since the concept clearly allows for innovative cell and stack architecture designs, it seemed reasonable to anticipate the work on interconnects, which required on the one hand long term testing regarding ageing and reactivity, and which, on the other hand, had to be thoroughly associated with any brainstorming on the architecture design of the central membrane. Therefore, substantial part of WP5 already started during this first period.

- Activities in WP2 and WP3 were mainly focused on powders synthesis and characterization (tasks 2.1 and 3.1 [start month: m1]), shaping processes preliminary work (tasks 2.2 and 3.2 [start month: m3]) leading to the first tests for the fabrication of symmetrical cell (tasks 2.3 and 3.3 [start month: m6]). As regards to tasks 2.1 and 3.1, some difficulties were encountered for the first six months in the sense that powders did not completely correspond to the specification required for the diverse shaping processes in view. However, rescue actions were undertaken in order to satisfy the requirements of the partners. After six months, convincing information was obtained on the capability of the consortium to shape both cathodic and anodic parts of the IDEAL-Cell. The set-ups for electrochemical testing (tasks 2.5 and 3.5 [start month: m8]) were also developed in order to characterize electrical response of symmetrical and pseudo-symmetrical half-cells (from tasks 2.3 and 2.4 in WP2 and tasks 3.3 and 3.4 in WP3). According to the Gantt chart, tasks 2.6 and 3.6 did not have to start yet, although some discussions already took place during the first year in order to anticipate them (i.e. to increase the adhesion between each layer by improving the quality of interfaces).

- Regarding WP4, activities on modelling (task 4.1 [start month: m1]), on reactivity of materials (task 4.2 [start month: m3]) and on the central membrane fabrication (task 4.3 [start month: m3]) gave rise to promising results. As first interesting results, modelling activities in task 4.1 focused on the water pressure drop and elimination process within the central membrane, and it was shown that probably large planar standard cell geometries will not allow to get rid of the water satisfactorily because of water vapour piling-up in pores. Chemical reactivity tests (task 4.2) carried out in vigorous conditions showed that components did not react with each other. In task 4.3, first tentative central membrane samples could be prepared with varying porosity. Results showed that a good control of the porosity was easily obtained by adding specific pore formers (graphite, starch) to the starting slurry. Regarding task 4.4, alternative and promising attempts were carried out, such as the first metal supported green IDEAL-Cell fabricated by tape casting.

- To anticipate Phase II, some activities of WP5 began, such as first tentative central membrane optimization (task 5.1 [start month: m25]), interconnects design (task 5.3 [start month: m25]), a design for an ASR measurement set-up (Real Life Tester) and some elements for their integration into a short-stack (task 5.4 [start month: m25]).

Year 2

The second year of the project was essentially focused on the implementation of experimental and modelling activities dedicated to the Proof of Concept within WP4, not all necessarily planned in the DoW (i.e. Proof of Concept samples and dedicated set-up coupled to a moisture analysis) but nevertheless requisite to overstep the Go/No Go decision.

- Activities in WP2 and WP3 were mainly focused on the synthesis of powders, shaping and testing of the oxygen and the hydrogen compartments. Spray-dried spherical-shaped particles containing LSCF40(48) (and La-deficient LSCF40(48)) powders (tasks 2.1 [start month: m1]) for plasma spraying activities were fabricated. "Standard" YDC15, LSCF40, LSCF48 and BCY15 powders (tasks 2.1 and 3.1 [start month: m1]) were continuously produced and adjusted by MT to supply the stock of partners involved in tape casting and screen printing activities.

Symmetrical cells were shaped via tape casting, screen printing and plasma spraying (the latter only for the oxygen compartment) (tasks 2.3 and 3.3 [start month: m6]). These symmetrical cells were electrochemically tested (tasks 2.5 and 3.5 [start month: 8]). Tasks 2.4 and 3.4 devoted to the fabrication of pseudo-symmetrical cells have been arbitrarily set back by the consortium insofar as they are of less pertinence with respect to the ones dedicated to the Proof of Concept, even if one of them was fabricated and being tested in month 25. The role of pseudo-symmetrical cells was to independently evaluate on the one hand the proton conductivity in porous BCY15, and on the other hand the oxygen conductivity in porous YDC15. It seemed to the consortium much more realistic to measure such parameters by feeding successively and independently a central membrane on the one hand with hydrogen, and on the other hand with oxygen. These electrochemical measurements were advantageously coupled to X-ray microtomography experiments (16th-19th of July, 2009) at ESRF in Grenoble on the central membrane. These extremely interesting and fruitful experiments were not planned in the initial DoW. Therefore, it seemed reasonable to postpone tasks 2.4 and 3.4 to the second phase of the project if they are still necessary (Optimization and Integration of the Dual Cell).

Within tasks 2.6 and 3.6 [start month: m2] some convincing work was carried out to increase the chemical and mechanical adhesion between each layer by improving the quality of interfaces (modifying slurries or inks composition for tape casting or screen printing processes respectively, abrasion or sandblasting of the surface of substrates, optimizing the powders quality as well as process parameters in spray drying).

As a conclusion about WP2 and WP3 at the end of the second year, all types of powders were successfully fabricated after adjustments, all samples were produced successfully by tape casting, screen printing and plasma spraying; all samples were tested except the pseudo-symmetrical cells. Electrochemical results show that the conductivities of YDC15 and BCY15 are excellent, that the couple YDC15/LSCF48 is excellent; but it showed also that some works had still to be done on the anode material, which exhibited deceiving performances associated with the presence of a resistive nanometric layer of Y2O3 at the interface between BCY15 grains, under investigation by analytical TEM-STEM.

- Regarding WP4, experimental (tasks 4.4 [start month: m12], 4.5 [start month: m14] and 4.6 [start month: m18] and modelling (tasks 4.1 [start month: m1]) activities were carried out to fabricate, test and model a full non optimized IDEAL-Cell. On this occasion, a simplified design of the dual cell (PoC samples) (task 4.4 [start month: m12]) was proposed, which consists in a central membrane (CM) sandwiched between both dense YDC15 and BCY15 electrolytes on the surface of which standard platinum electrodes were deposited: they were fabricated via several processes (task 4.5 [start month: m14]), some not planned in the original DoW such as spark plasma sintering (SPS) and hot pressing (HP) and electrochemically tested (task 4.6 [start month: m18]) at 600 °C using H₂ and O₂ respectively on the anode and on the cathode sides of the cell, via a dedicated three independent chambers set-up developed to detect and measure the water produced within the central membrane during operation.

Electrical measurements established that the simplified PoC samples operated as a high temperature fuel cell with a behaviour characteristic of the device configuration itself. Proof of Concept criteria were defined, and PoC samples have successfully verified them. Lately, a full IDEAL-Cell obtained by cold pressing and tape casting showed the same electrochemical behaviour. On the other hand, an electrochemical macrokinetic model (tasks 4.1 [start month: m1]) was developed to precisely describe the electrical behaviour of the simplified PoC samples and simulation results show that the resulting polarization curve was mainly driven by the central membrane, not by the electrodes which showed very little overpotential losses, as it was expected when the concept was invented in order to eliminate the presence of water at electrodes. Activities regarding PoC samples were not focused on the geometry (layers thickness ranged between centimetres for the HP PoC samples, and millimetres for the SPS samples) and microstructure optimization, but rather on their robustness; therefore the measured performances are evidently low.

Modelling told us which were the pertinent geometrical, morphological and microstructural parameters to play with in order to optimize the electrical performances (thickness of components, tortuosity and

percolation pathways of both porosity and BCY15, YDC15 active phases, the active triple phase boundary [TPB] segments length or volume density, the permeability...).

Activities on the central membrane fabrication (task 4.3 [start month: m3]) gave rise to promising results: several central membrane samples were prepared by tape casting with varying porosity (shape, size, amount) and proportion (in vol.%) of active phases (BCY15 and YDC15). The morphological parameters could be successfully extracted from X-ray microtomography 3D images analyses. The data were collected at the ESRF (European Synchrotron Radiation Facility) and obtained by scanning the sample in rotation with a high energetic X-ray beam. Results showed that a good control of the porosity over a wide range was easily obtained by adding dedicated pore formers to the starting slurries.

The effective properties of the central membrane were effectively predicted from the morphological data and the resulting electrical behaviour was validated by injecting the appropriate morphological parameters into the electrochemical model developed in parallel. A complementary modelling approach by CFD was implemented to optimize the microstructure of the central membrane (CM) for an efficient removal of the water from the cell: results revealed that a channelled or patterned type structure of the central membrane should significantly increase the efficiency of water removal, hence diminish strongly the concentration overpotential in the central membrane. Experimentally, this objective could be realized by adding an organic template/grid, having the shape of the desired channelled configuration, to a well-calibrated CM powder.

A new strategy to prepare the composite CM powders in one step through a mixed starting precursor, that is to say without mixing both BCY15 and YDC15 electrolyte powders, was attempted within task 4.3 by the decomposition of a Ba-deficient BCY15 phase. This strategy was thought to allow attenuating the difference of sintering behaviour between both BCY15 and YDC15 phases and highly increasing the density of triple phase boundary segment length per unit volume. This approach was started in WP4, but the consortium considered that this work was an anticipated part of task 5.1 dedicated to the central membrane optimization and forming of the optimized dual cell.

Activities on reactivity studies (task 4.2 [start month: m3]) were completed and allowed defining precise thermodynamic sintering and operating conditions within task 5.3 (optimization of operating conditions).

As a conclusion of the second year and regarding works achieved in WP4, simplified PoC samples and full IDEAL-Cells were obtained and electrochemically characterized; they all verified the PoC criteria defined in agreement with our Advisory Board (i/ stable OCV; ii/ stable polarization curve; iii/ complex impedance signature of water formation; iv/ detection and quantification of water formation in the central membrane). The polarization curve fitted well our electrochemical modelling when experimental data were introduced in the model; owing to millimetre to centimetre thicknesses, the measured external current was low, in the range of 1.0 to 10 μA , but the possibilities of optimizing the central membrane morphology and microstructure were under control, especially via the highly relevant outcomes from the high resolution X-ray microtomography measurements and the modelling. In other words, it was proved after the second year of the project that IDEAL-Cell was a real operating fuel cell.

- Even if not planned to start before the onset of year 3, the activities in WP5 have unquestionably begun insofar as first results had been obtained on the central membrane and dual cell optimization (task 5.1 [start month: m25]) (see results in task 4.3), as well as interconnects design (task 5.3 [start month: m25]). A set-up for ASR measurements (Real Life Tester) and some elements for their integration into a short-stack (task 5.4 [start month: m25]) came out during this second year. Modelling activities within tasks 4.1 and 4.3 had already allowed defining which experimental conditions should be the best for an optimal functioning of the dual cell that would be fine-tuned in WP5. Moreover, a new interconnect design for an IDEAL-Cell stack had taken shape (proposed during the "Cell Testing & Design and Interconnect" meeting in Stuttgart, the 10th of December, 2009) and was supposed to be more efficient for water evacuation and limit the surface of metallic components facing aggressive atmospheres. The consortium had considered that it was essential to anticipate these long term tasks, and especially all those dedicated

to the ageing and testing of the interconnects, in order to start the second phase of the project in the most efficient possible way.

As a conclusion, WP5 was not supposed to start before month 25, but some of its long term activities needed to be anticipated, i.e. the fabrication of an original interconnect tester (Real Life Tester) for the evaluation of the interconnect behaviour in its real environment (respectively oxidizing and reducing atmospheres on one side and on the other), the onset of the central membrane optimization, elements of integration design and modelling.

Year 3

Subsequent to the mid-term review of the IDEAL-Cell project (Genoa, March 23rd, 2010) for Phase I, the European Commission recommended (April 26th, 2010) the consortium to slightly re-direct their final objectives for the last two years (Phase II), to focus more on understanding the basic mechanisms at stake in this new concept, and enhancing the electrochemical performances rather than integrating it into a short stack. This new direction led the consortium to continue working on some tasks (2.2, 2.3, 2.5 in WP2; 3.2, 3.3, 3.5 in WP3; 4.1, 4.3, 4.4; 4.5, 4.6 in WP4) only planned to run in Phase I at the time the Description of Work (DoW) was written.

- Activities within WP2 and WP3 were mainly focused on routine synthesis of (i) standard powders for shaping facilities, i.e. tape casting and screen printing, (ii) granulated (composites or not) powders (tasks 2.1 and 3.1) for plasma spraying deposition, (iii) nanometric BCY15 powders (task 3.1) to better design the central membrane architecture, (iv) shaping processes for the fabrication of symmetrical cells (tasks 2.3 and 3.3) using more efficient composite electrodes as LSCF48/YDC15 or LSCF48/BCY15 and (v) electrochemical characterization by Differential Impedance Analyses (tasks 2.6 and 3.6). Concerning tasks 2.4 and 3.4, devoted to the fabrication of pseudo-symmetrical cells, the consortium has decided to take them out from the workplan and primarily focuses more on optimizing the central membrane within task 5.1. The idea of feeding a porous central membrane directly with hydrogen or oxygen to measure the proton or oxide-ion conductivity was found to be much more realistic than any testing of pseudo-symmetrical cell.

- Regarding WP4, activities on the central membrane fabrication (linked to task 5.1) gave rise to promising results. In task 4.3, central membrane samples were successfully prepared with (i) channelled architecture along with varying nature of porosity (proportion in vol.%, size and shape) and (ii) different proportion (in vol.%) of solid phases (BCY15 and YDC15).

Within WP4, an extremely important result was obtained: BCY15 was found to exhibit a mixed conduction: at 600 °C the level of protonic conduction when BCY15 is fed with hydrogen is equivalent to the level of anionic conduction when fed with oxygen; this results opened the route for a drastically easier shaping of the cell (both electrolytes and the central membrane could then be made of the same BCY15 material, with minimized shrinkage and thermal expansion mismatches), and for much improved performances (triple phase boundary segment in the initial design become surfaces of pores in the central membrane, then increasing drastically the reaction site, hence the exchange current and therefore diminishing strongly the activation overpotential associated with the central membrane). This new development of an IDEAL-Cell based only on the mixed conduction BCY15 material was patented by those of the partners involved in this finding (ARMINES, IEES and CNR) under the name “Monolithic Concept”.

- Activities within WP5 had been anticipated by several months as already mentioned in the report of Year 2 works above. Preliminary results were obtained on (i) central membrane optimisation (task 5.1), (ii) interconnects design (task 5.3), (iii) a design for ASR measurements (Real Life Tester), and (iv) some elements for their integration into a short-stack (task 5.4).

Concerning the first point (i), the idea of implementing a cross-linked channel-shaped porosity in the CM was regarded as a potentially effective way to facilitate convection and then evacuation of water out of

the CM. X-ray microtomography experiments carried out at the ESRF (October 19th-21st, 2010) showed that a good control of the porosity network was easily obtained by adding polymeric meshes in dip coated or tape cast layers. In addition, the transversal and lateral vapour permeabilities of selected CM (from Phase I, without channels) were measured using different nature of gases.

Regarding the EC comments and recommendations, the modelling activities have been conducted to support the cell design (see task 5.3) and central membrane development (see task 5.1) in view of improving electrochemical performances; for that purpose, the electrochemical model of IDEAL-Cell was continuously enhanced with the implementation of experimental data. In order to improve the central membrane microstructure, nano-size BCY15 powders, synthesised by a microwave assisted sol-gel process, were being fabricated. Moreover, laboratory scale syntheses of new composition of electrolyte (e.g. In-doped BaCeO₃) was performed.

Concerning the fabrication of an optimized dual cell, some extensive works were started to improve performances of the cathode and anode compartments (parts of the tasks 2.3 and 3.3). Within task 5.3, promising new cell concepts based on the IDEAL-Cell architecture were reported. The potentiality of the RLT for ageing tests, performed on selected steels and cells, was reported within task 5.4. A large quantity of YDC15/NiO granulated composite powder was produced for the fabrication of a YDC15-based ITSOFC anode in the frame of the comparative study in task 5.5.

Year 4

The fourth year of the project, following the EC recommendations, was essentially dedicated to tasks achieved within WP5, on the central membrane optimization and forming of the optimized dual cell (task 5.1), on modelling and optimization of operating parameters (task 5.2 and task 5.3), on the development of cells, cell integration and cell stack design (task 5.4), on the comparative study with YDC based SOFC and BCY15 based short stacks (task 5.5 and task 5.6).

The electrochemical and mathematical theoretical model developed before has been validated and enriched with data resulting from the proof of concept experiments and from cells developed in task 5.1, especially monolithic cells to which the model has been adapted (with nevertheless account not taken of the increase of reaction site number compared to standard CM). Along with extensive use of impedance spectroscopy the model applied to IDEAL-Cell showed that (task 5.2), as anticipated, there was a drastic decrease of the overpotentials associated with the electrodes, and that electrical losses were almost totally restricted to overpotentials occurring in the central membrane.

The central membrane is therefore the limiting component for the optimal operation of the device (in standard SOFCs and PCFCs, the limiting components are the electrodes) on which most of the efforts during the last two years were focused. The losses in the central membrane are ohmic, activation and concentration overpotentials, but it was shown that the monolithic concept could reduce significantly these losses. Calculation showed that a thickness of the order of 120 μm was a good compromise for it diminishes the ohmic losses, did not lower significantly the exchange current (that is linked to the TPB – or pores surface in the monolithic concept-, and then to the activation overpotential) and still does not build up too much pressure while allowing an easy escape of water molecules (playing on the concentration overpotential) (task 5.2 and task 5.3).

It was found that the best compromise for the operating temperature (and the range of temperature where the IDEAL-Cell concept brings the most compared to sister concepts) was 600-700 °C, and especially for the monolithic concept for which it was experimentally and theoretically demonstrated that the transport number for protons and anions was 0.5 at 600 °C (task 5.4). This, along with fast increasing performances (1 mW cm⁻² in early 2010, increasing step by step to 130 mW cm⁻² in late 2011 for still thick samples and non-fully optimised cells, or for full plasma sprayed cells) (task 5.4), confirmed the basic idea of the IDEAL-Cell concept on which the project was built, that stated that avoiding the presence of water at electrodes was a significant technological improvement.

Finally, the consortium has compared the performances of IDEAL-Cell fabricated via two major processes, on the one hand by a sequence of standard ceramic processes (tape casting, cold pressing and/or screen-printing) and on the other hand via plasma spraying, with a SOFC and a PCFC counterpart made exactly with the same processes and hence with the same or comparable geometry (diameter, thickness). These comparisons are the object of a specific deliverable dedicated to the IDEAL-Cell technical benchmarking (D 6.4). Under these conditions, it is shown that IDEAL-Cell obtained via standard ceramic processes (still 1.2 mm thick) exhibits significantly better performances than PCFC and SOFC with the same geometry, and extrapolation based on a decreased thickness and associated resistance drop for the electrolyte reaches 800 mW cm^{-2} ; regarding plasma sprayed samples, it is seen that IDEAL-Cell behave significantly better than PCFC, but performances remain slightly lower than those of SOFC deposited by this technique. It is to be noted that the samples obtained by plasma spraying are still “first shots” samples that still present observable defects (porosity, microcracking), and also that SOFC with high performances are routinely obtained by plasma spraying, and especially at DLR where these experiments were carried out; nevertheless, the results are highly promising and have demonstrated that IDEAL-Cell can be obtained via an easily marketable process.

Considering all the results, experimental and theoretical, obtained in the course of the project, it is clear that IDEAL-Cell is a viable and potentially very interesting concept. Two years after the proof of the concept, the performances that are attained are potentially of the order of those of well established high temperature fuel cells, but with none of their drawback. IDEAL-Cell is also shown to be perfectly reversible, which in turn could be a key asset in particular when coupling to an intermittent renewable energy source.

General vision, highlights of the project

Four years ago, IDEAL-Cell was just a crazy schematic doodled in the corner of a blackboard. It must be strongly emphasized that after 2 years the concept was experimentally proved, and after 2 more years the performances are better to that of PCFCs and SOFCs at 600-700 °C under comparable geometries. It must also be emphasized that the fuel cell community has been working for about 50 years on SOFCs, and for about 25 years on PCFCs. Therefore, as far as maturity is concerned, one must compare 50 and 24 to 2 years for heading towards potentially comparable performances. This is an extraordinary accomplishment.

To mark out this accomplishment, a number of challenging issues had to be achieved:

- establish proof of concept criteria;
- develop dedicated specific testing set-ups;
- realize a first prototype and test it on a dedicated set-up for the proof of the concept;
- shape the cell by the most appropriate processes or sequence of processes;
- understand the new mechanisms at work;
- model theoretically the cell (kinetic, charge and mass transfer, morphology...);
- develop a specific interconnect material and design;
- increase the performances;
- compare those performances with that of SOFCs and PCFCs obtained under “comparable” conditions.

A number of excellent results were recorded, either on the improvement of electrode (with composite composition), electrolyte and interconnect materials, via dedicated testing (i.e. Differential Impedance Analysis, 2-atmosphere or 3-chamber testers, X-ray microtomography and 3D mathematical morphological reconstruction) or on the fundamental understanding of the mechanisms at work (via kinetic, mass and charge transfer and mathematical modelling). Most of these advances were either published or presented at conferences, or both.

Some of the challenges listed above were real key issues (proof of the concept, increase of performances, comparison with existing technologies...) and some results, unexpected (mixed conductivity in BCY15, reversibility of IDEAL-Cell with a new mechanism of conduction), were either highlights that boosted the

concept (mixed conduction of BCY15 led to the monolithic concept with a drastic improvement of performances) or milestones that opened new potential applications (the monolithic IDEAL-Cell, thanks to its high symmetry and properties, showed a remarkable ability to work also as an electrolyser). The following sections will focus on these specific steps that have highlighted the course of the project.

Proof of the concept

Obviously, to prove that the IDEAL-Cell configuration was a real operating high temperature fuel cell was the first step to overcome. It was an extraordinary challenge to which all the efforts and resources of the consortium have focused during the two first years of the projects, setting materials, criteria, new set-ups, new formalisms. This essential step was the object of a GO/NO GO decision that fortunately turned to be a GO decision.

Experimental proof of the IDEAL-Cell concept required that the cell behaved electrochemically like a fuel cell and that water produced from the recombination of ions was present within the central membrane during cell operation. The last point was quite delicate since BCY15 needs water to function; therefore just “additional” water formation had to be detected and cross-correlated to other more straightforward criteria to prove the concept. It was then inferred that the proof of the IDEAL-Cell concept could be evaluated through 4 criteria:

- (i) a stable OCV under hydrogen and air;
- (ii) a stable polarization curve (V/I);
- (iii) a specific impedance fingerprint for the appearance of water;
- (iv) clear and direct evidence of water in the central membrane.

The first experiments were performed on 3 mm thick multilayered cells made of a mixed $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ + $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ porous central membrane sandwiched between dense $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ and $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ electrolyte layers. Such structures were prepared by Spark Plasma Sintering (SPS). The sintered ceramics, 10 mm in diameter and 3 mm thick, were annealed in air at 650 °C for 10 h in order to remove graphite from the central membrane and excess oxygen vacancies possibly produced during SPS. Figure 2 shows a lateral view of an SPS pellet after annealing.

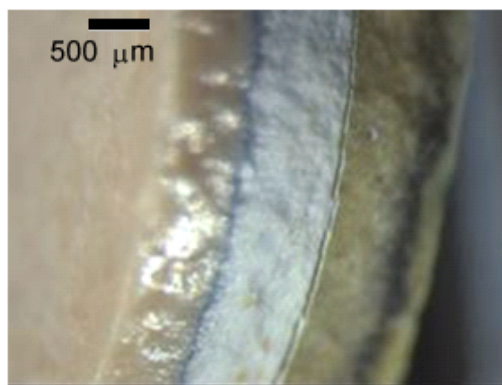


Figure 2. Three-layer sample fabricated by SPS. Left to right: YDC15-CM-BCY15.

Circular Pt electrodes (0.12 cm^2) were formed on both sides by brushing a Pt-ink (Metalor) and curing at 1000 °C. The cells were tested in a two-electrode configuration at atmospheric pressure. Oxygen and hydrogen diluted with nitrogen in different ratios were fed to the cathodic and anodic compartments respectively. The anodic gas mixture was bubbled in water at 25 °C for humidification. The cell was placed on the top of an alumina tube and sealed to ensure a separate gas-tight anodic compartment. Another alumina tube with a dead end was fitted to the previous one to form the cathodic compartment.

Pt meshes were placed at both sides of the cell. The alumina tubes together with thermocouples and Pt wires, welded to the Pt meshes, were connected to a metal support (Probostat, NorEcs) along with gas and electric connections. A schematic of the measurement rig assembly is given in figure 3, together with an image of an SPS three-layer sample sealed on the supporting tube of the measurement rig. The alumina part of the cell rig was placed in a tubular furnace (Carbolite). Chronopotential, polarization and impedance measurements were carried out using a potentiostat-impedancemeter (Autolab, Pgstat30).

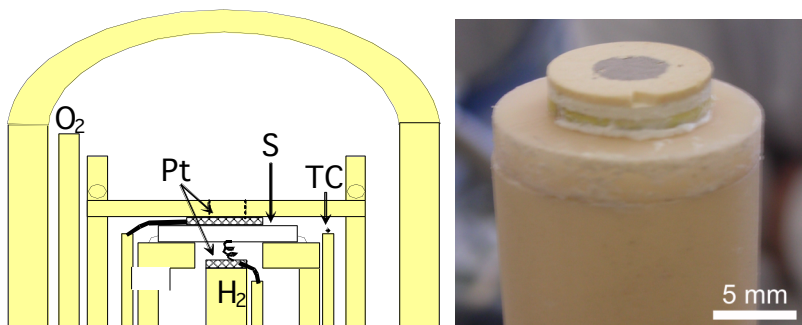


Figure 3. Schematic of the measurement rig (left) and sample sealed on supporting tube (right). *S* = sample, *TC* = thermocouple, *Pt* = platinum mesh, *H₂/O₂* = supplies.

Samples were heated to 900 °C under N₂ in order to cure the ceramic sealing paste supply and “switched-on” by applying wet H₂ and dry O₂ gases to the anodic and cathodic compartments respectively. The cell voltage under open circuit (OCV) conditions was recorded down to the test temperature (600 °C). Figure 4 represents the OCV value over an interval of 40 minutes at 600 °C, indicating a stable value close to 1.0 V. The inset shows the switch-on at 900 °C, with quick (less than 1 min) stabilization at the equilibrium value (0.75 V).

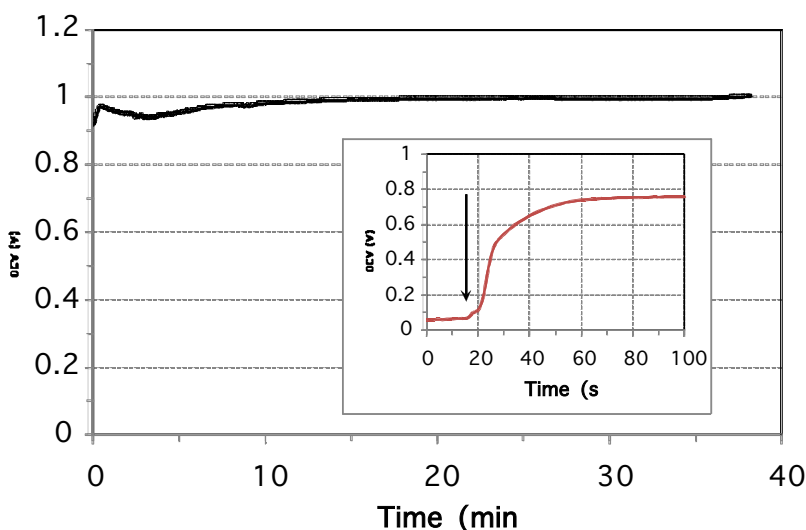


Figure 4. Open circuit potential vs. time at 600 °C for a three-layer sample. Inset: OCV across the switching from a N₂-N₂ to a H₂-O₂ supply at 900 °C, indicated by the arrow.

Polarization measurements were carried out in both potentiostatic and galvanostatic modes. One example, collected at 600 °C under H₂-O₂ gases, is given in figure 5. The response was reproducible and sensitive to partial pressure of the gases, as it is expected from a standard fuel cell. At low current densities the cell behavior is strongly governed by activation mechanisms. The specific power output was relatively low in all cases.

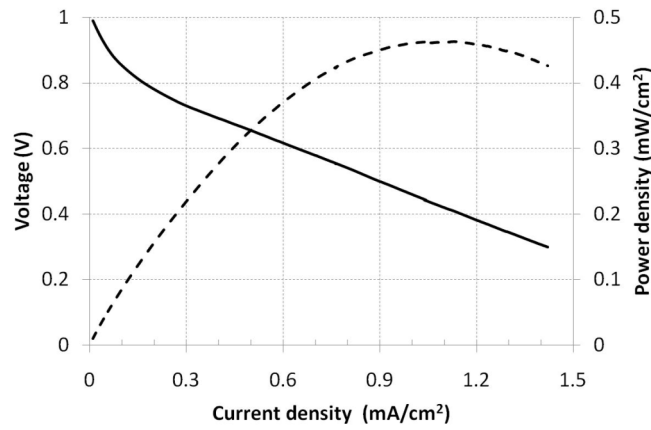


Figure 5. Cell voltage (solid) and power density (dashed) curves vs. current density obtained at 600 °C (H_2 - O_2).

The low activity of the electrodes used, the very thick dense electrolyte layers and the non-optimized dual membrane negatively affect the cell performance. However, the emphasis during the first stage of this study falls on proving the IDEAL-Cell concept with the simplest cell design and the highest robustness possible. Our second target consists in determining a general frame of realistic experimental parameters, which will serve as a basis for the extensive modeling activities that are in progress on the IDEAL-Cell design.

Impedance measurements were carried out at different temperatures, gas concentrations and under polarization. Methodological experiments were performed on cathode and anode half cells obtained by different shaping techniques. The observed results correlate well with similar measurements presented in the literature. The present analysis aims at a deeper understanding the impedance behavior of the new cell design in relation to the proof of the water formation. The absolute values of impedance are consistent with the d.c. measurements, *i.e.* the total resistance of the samples is in the range of kW at 600 °C.

An interesting feature was observed under large perturbation signal. Figure 6 reports impedance spectra in the complex plane representation collected at 600 °C with H_2 - O_2 supply in galvanostatic mode.

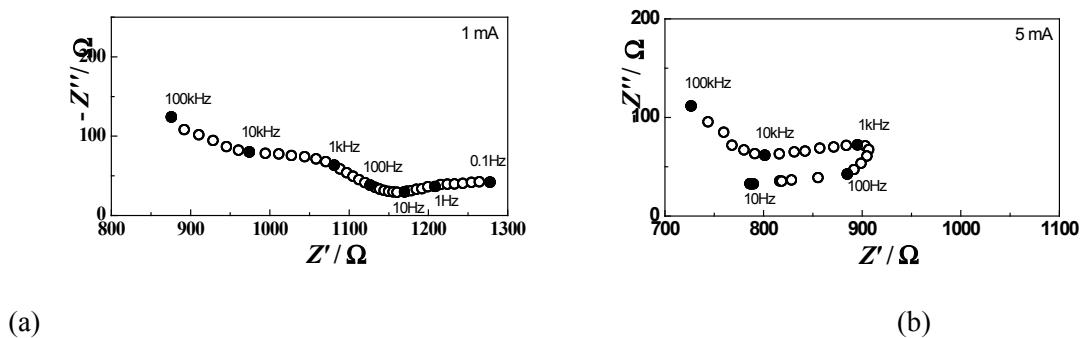


Figure 6. Complex plane impedance diagrams of a three-layered sample measured at OCV at 600 °C in galvanostatic mode at different perturbation amplitudes.

At lower perturbation signals (0.5 mA to 1 mA) the impedance diagrams feature three arcs (Figure 6a). When applying a larger perturbation signal (5 mA), the impedance diagram shows a “negative” arc with respect to the differential resistance, *i.e.* decreasing values of the real part of the impedance (Z') with increasing time of perturbation and quantity of electricity passing through the cell for half period (Figure 6b). Similar phenomenon (smaller negative arcs) has been reported in the literature for other systems and observed in our measurements of cathodic and anodic half-cells.

The mathematical explanation of this result is developed on a two-step reaction model. When the reaction rate coefficient of the second step (last arc in our case) is higher than that of the first (previous) step, the impedance diagram has a “negative” arc. From a phenomenological point of view this behavior could be related to the formation and growth of a new phase – in our case that should be the water formation. When the clusters of the new phase are small, *i.e.* under the critical size, the differential resistance is positive. When the clusters reach the critical size, their further growth becomes a spontaneous process, which is presented in the impedance diagrams with “negative” differential resistance, *i.e.* they continue to grow with smaller external energy. This explanation follows the classical Gibbs theory for formation and growth of new phases. It has been experimentally confirmed in electrochemical investigation of monoatomic (2D) phase formation, in new phase formation studies at the electrodes of classical lead-acid batteries, in corrosion of metals etc... In our experiments the formation and growth of the new phase becomes visible from an impedance point of view at large enough perturbation signals in the low frequency range, since those conditions ensure for half period the necessary quantity of electricity for the formation of a larger number of overcritical clusters of the new (water) phase.

Finally, measurements dedicated to the detection of the water formed within the central membrane were performed. It is seen on figure 7 that the humidity detected in the third chamber decreased until the current started to flow. The increase of the water signal in the central membrane continues probably due to the small driving force for the diffusion of water from the CM to the third chamber and also because the transfer function of the whole system probably exhibits a certain hysteresis (the system has lots of surfaces on which water can adsorb and desorb, including the central membrane microstructure and the rig, giving some viscosity to the overall dynamics of the water detection). However, after a stabilization of the moisture analyzer signal and as the polarization was switched on again, a further increase of the humidity detection was observed. This cell is characterized by an extremely low current flow when loaded; nevertheless a clear signal of the water formation has been observed.

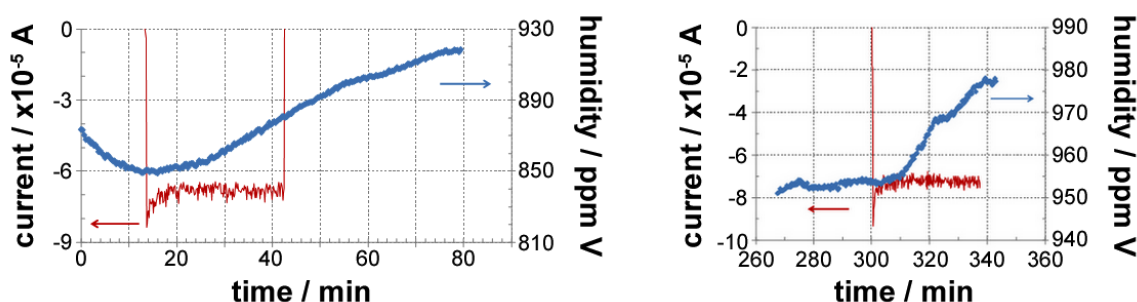


Figure 7. Current and water formation under 300 mV polarization for different times

This experiment has been carried out many times on samples of different shaping origins. The one presented above was one of the first proof of concept experiment achieved on a very rustic and robust sample. In spite of poor performances due to non-optimized geometry, materials and microstructures, it has demonstrated that all the criteria defined for proving the IDEAL-Cell concept were fulfilled: (i) a very stable OCV close to 1 V typical for the electrochemical potential of water formation from hydrogen and oxygen was recorded (for long duration), indicating that the rig and samples were gas tight; (ii) a stable and reproducible polarization curve of a typical high temperature fuel cell was recorded, exhibiting a sensible behavior to variation of partial pressure of gas supply, as it is observed in standard fuel cell systems; (iii) a complex impedance fingerprint specific for the formation and growth of a new phase was observed at high current perturbation, which could be attributed to the generation of water in the central membrane; (iv) the direct evidence of “additional” water in the central membrane compartment directly related to the current flowing across the cell.

The monolithic concept

The BCY15 electrolyte was investigated separately on symmetrical electrolyte supported half cells with metal (Pt, Ag) electrodes. The measurements were carried out in the 200-700 °C range of temperature in hydrogen (diluted with nitrogen or argon) and in air/oxygen for evaluation of the additional oxygen conductivity which should be present, since the activation of the proton conductivity needs oxygen vacancies. For more precise determination of the BCY15 resistivity and activation energy, a correction of the measurement rig parasitic inductance and resistance and data analysis by Differential Impedance Analysis (DIA) were performed for some of the experiments.

The results obtained for the BCY15 proton conductivity are presented in figure 8 and table 1. They are compared with data from the literature. It can be concluded that the produced BCY15 is in the group of the best materials in respect to the proton conductivity; it is even the best ceramic material of known composition above 500 °C.

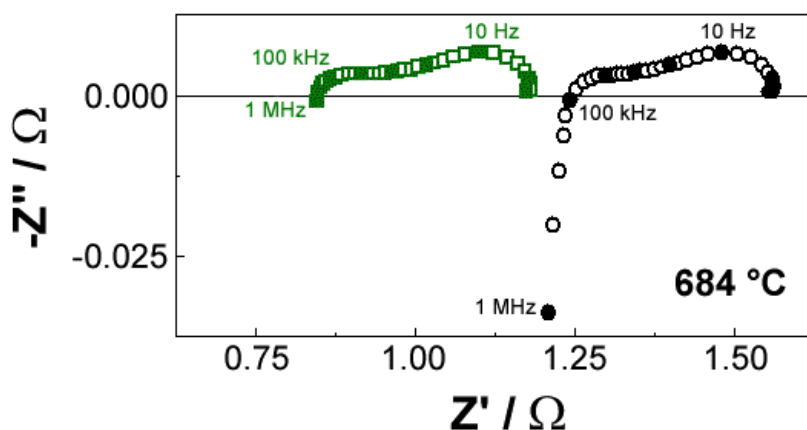


Figure 8. Complex plane impedance diagrams of half- Ag/BCY15/Ag cell (●) before and (■) after correction for parasitic resistance and inductance.

Table 1. Conductivity of BCY15 at temperatures 500-700 °C compared with data from the literature.

Electrolyte composition	σ at about 500 °C / S cm ⁻¹	σ at about 600 °C / S cm ⁻¹	σ at about 700 °C / S cm ⁻¹
BCY15 from the project*	3.60×10^{-2} **	6.60×10^{-2} **	1.26×10^{-1} **
Unknown composition	-	8.70×10^{-2} (550 °C)	1.00×10^{-2}
Sr(Ga _{1.1} Nb _{0.9})O ₆	-	1.80×10^{-2}	-
Sr(Nd _{1.1} Nb _{0.9})O ₆	-	3.60×10^{-2}	-
Sr(Sc _{1.1} Nb _{0.9})O ₆	-	3.20×10^{-3}	-
Ba ₂ In _{1.6} O _{5.2-δ/2} (OH) _δ	3.50×10^{-3}	5.50×10^{-3}	1.00×10^{-2}

* best results; ** estimated by DIA.

Since both BCY15 and YDC15 are also operating together in one compartment (central membrane), it is useful to compare their resistivities to look for an optimized design of the central membrane. As it could be expected, the proton conducting material has a lower resistivity than its anionic counterpart. The difference decreases when the temperature increases, probably because of the increasing concentration of oxygen thermal vacancies in the oxygen conductor. For the best samples at operating temperatures in the range 600-700 °C, the resistivity of BCY15 is about 5 times lower (figure 9).

The measurements of the half-cell in oxygen atmosphere show resistivity which is similar to that obtained in wet hydrogen for temperatures 500-700 °C (figures 10 and 11). This important result clearly shows that BCY15 exhibits a mixed conduction: the material is an excellent proton conductor when fed by hydrogen, and an excellent oxygen conductor when fed with oxygen. The consequence of this result was immediately used by the consortium to develop the concept of monolithic IDEAL-Cell (patented in 2011)

in which both hydrogen and oxygen electrolytes are made of dense BCY15, and the central membrane is made of porous BCY15. In addition, our works showed also that both electrodes of IDEAL-Cell could be a composite (BCY15 + Ni for the anode, BCY15 + LSCF48 for the cathode). It has tremendous consequences, as already mentioned:

- shaping is made drastically easier (diminishing of differential shrinkage and expansion or contraction during thermal treatment);
- thermomechanical ageing is reduced (again because of a diminished differential thermal expansion coefficient);
- chemical ageing is also strongly reduced (much less chemical gradient, hence diffusion driving force across the cell);
- increased performances (TPBs become CM pores surface, hence drastically increasing the reaction sites number, and then the exchange current, leading to a strong diminishing of the CM activation overpotential);
- decrease of the CM internal resistance (ionic transport pathway tortuosity diminished).

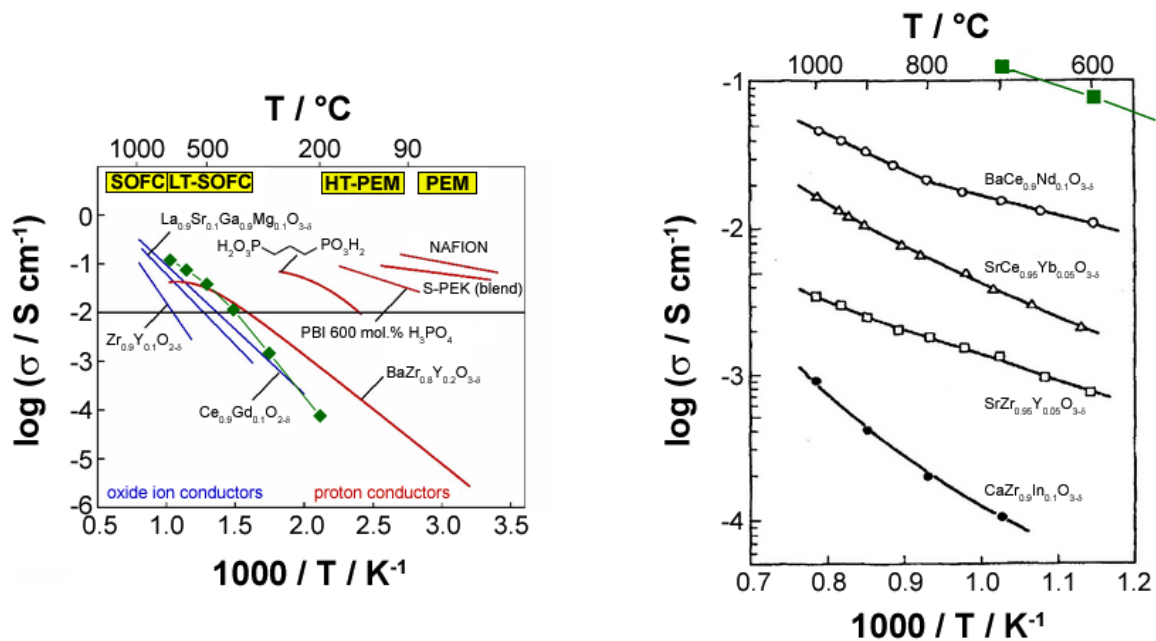


Figure 9. Comparison of the BCY15 proton conductivity (■) with data from the literature.

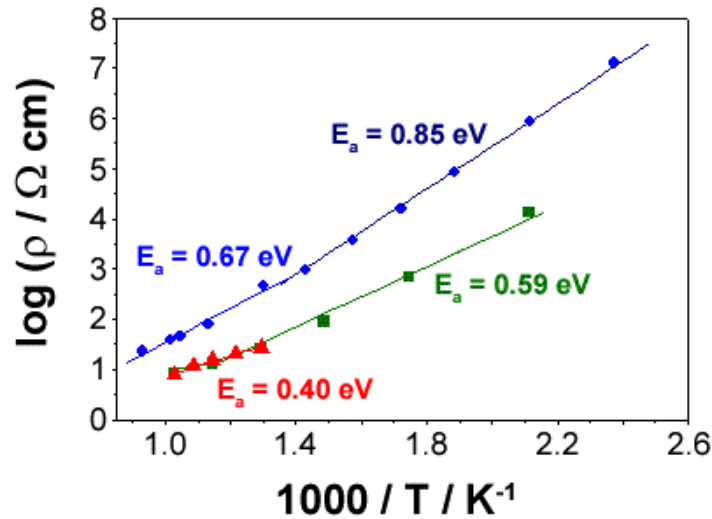


Figure 10. Arrhenius plots for the total resistivity of BCY15 in (▲) hydrogen (wet) and (■) oxygen and (●) for YDC15 in oxygen.

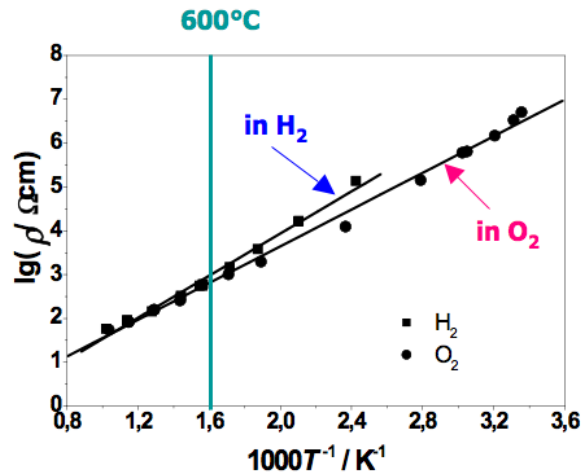


Figure 11. Arrhenius plots for the resistivity of BCY15 in hydrogen (wet) and oxygen.

Increase of performances, projection for thinner cells

In year 3, the monolithic approach (see above) was introduced based on a systematic study of BCY15 conductivity in both hydrogen and oxygen atmospheres. Obviously the monolithic dual membrane approach can be regarded as an original and effective optimization tool which could reduce the above mentioned problems, some of them typical for every fuel cell design. It also simplifies the technological procedure for preparation of the dual membrane configuration.

The electrolytes-central membrane assembly (ECMA) of the monolithic button cells was prepared by single stage cold pressing and sintering. Pt electrodes were deposited by slurry coating following the procedure of the Pt ink producer. In year 4, a second generation of improved monolithic BCY15-based model cells were produced and tested. The thickness of the second generation ECMA was about 1.0-

1.1 mm. Microscopic observation showed that the 3 ECMA layers are not of homogeneous thickness. The estimated mean values are: dense BCY15 (~ 0.4 - 0.5 mm), porous BCY15 (~ 0.2 mm), dense BCY15 (~ 0.4 mm).

The produced cells were tested in different operating conditions: (i) temperature range 500-800 °C (figure 12); (ii) different gas flow and pressure (figure 13). Single gas feeding was preferred due to the registered in year 3 influence of the molecular weight on the gas permeability in porous media.

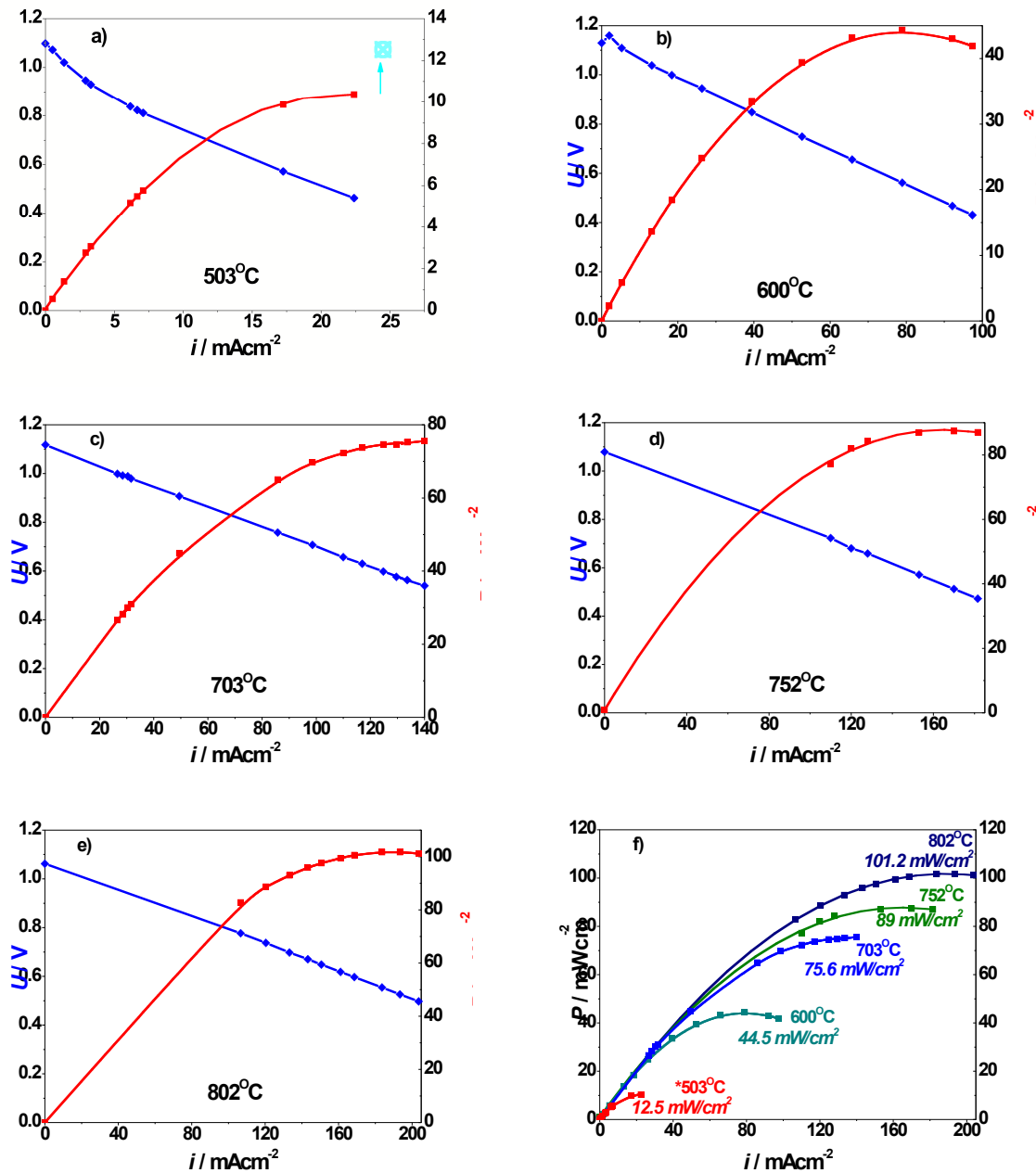


Figure 12. Current density/voltage curves and power density of monolithic cell (second generation, thickness 1.1 mm) as a function of the temperature at a constant gas flow (90% wet hydrogen and 90% oxygen (144 mL min^{-1})). The gas flow in (a) is 10% wet hydrogen and air; at $\otimes$ the gas flow is 20% wet hydrogen and 20% oxygen.

The performed tests at different operating conditions showed that the best results for the whole temperature interval were registered at the highest flows of oxygen and wet hydrogen (figures 13 and 14). The dilution of the hydrogen with argon and the replacement of oxygen with air (keeping constant gas flows) reduce P_{max} with more than 30% (figures 13a and 13b). We suppose that in addition to the

decreased pressure of the reacting gas, the different permeability which is proportional to the molecular weight is also a factor for the deterioration of the performance. Especially for the mixture H_2/Ar where the difference in the molecular weights of the two gases is very big, the so called "pillow" effect could additionally decrease the gas supply and thus the power.

The results obtained on the monolithic dual membrane cell are very promising (figure 12f). The best power densities, reached at gas flow wet H_2 90% and O_2 90%, are: 44.5 mW cm^{-2} at 600°C and 75.6 mW cm^{-2} at 700°C for ECMA thickness 1.1 mm. The impedance measurements ensured separation of the ECMA resistance and the polarization resistance (figure 15). It can be accepted that the polarization resistance, which is about $0.3 \text{ } \Omega \text{ cm}^{-2}$, is independent on the ECMA thickness. Then a recalculation of the total cell resistance for thinner layers, as well as of the maximum power density can be done (table 2, figure 16). The results are extremely encouraging – the values exceed the best experimental results reported in the literature for PCFC studies.

Table 2. Recalculated maximum power density P_{max} for thinner configurations of the monolithic cell based on the measured data at 700°C .

Thickness / μm	R_{ECMA} / Ω	R_{el-des} / Ω	R_{cell} / Ω	$R_{cell} / \Omega \text{ cm}^{-2}$	$P_{max} / \text{mW cm}^{-2}$
1100	7.90*	0.5*	8.4*	3.62	76*
660	4.74	0.5	5.24	2.25	122
330	2.37	0.5	2.87	1.24	222
100	0.72	0.5	1.22	0.525	524
50	0.36	0.5	0.86	0.37	743

* measured.

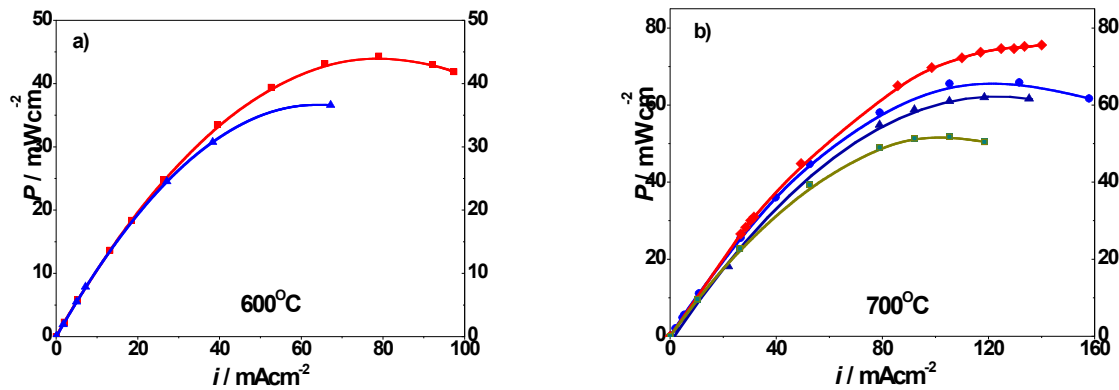


Figure 13. Dependence of P_{max} on the gas feeding for monolithic cell (second generation, thickness 1.1 mm): (a) wet H_2 / O_2 – ($\blacktriangle$) 20% / 20%, ($\blacksquare$) 90% / 90%; (b) 10% wet H_2 + 80% Ar / 90% air – ($\blacksquare$); wet H_2 / O_2 – ($\blacktriangle$) 20% / 20%, ($\bullet$) 20% / 90%, ($\blacklozenge$) 90% / 90%.

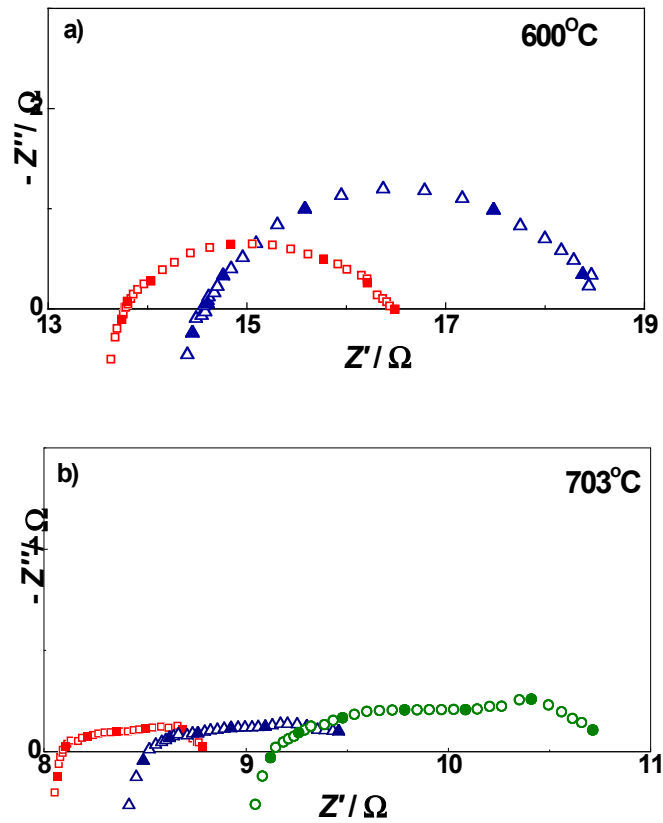


Figure 14. Complex plane impedance diagrams of loaded monolithic cell (second generation, thickness 1.1 mm) at different gas feeding: (a) wet H_2 / O_2 – (▲) 20% / 20%, (■) 90% / 90% (load 15 mA); (b) 90% wet H_2 / 90% O_2 – (■), 10% wet H_2 + 80% Ar / 90% O_2 – (▲), 10% wet H_2 + 80% Ar / 90% air – (●) (load 50 mA).

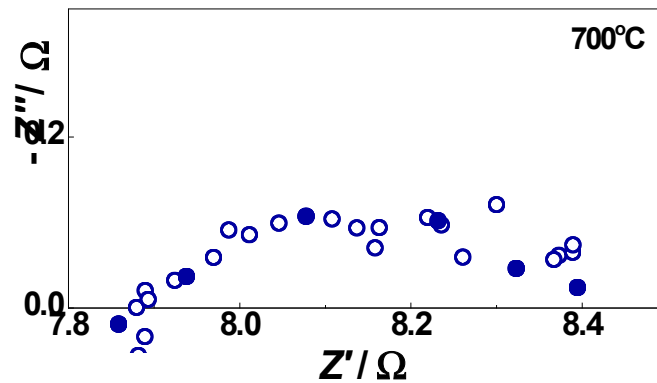


Figure 15. Complex plane impedance diagram of monolithic cell at OCV (second generation, thickness: 1.1 mm, surface: 0.43 cm^2).

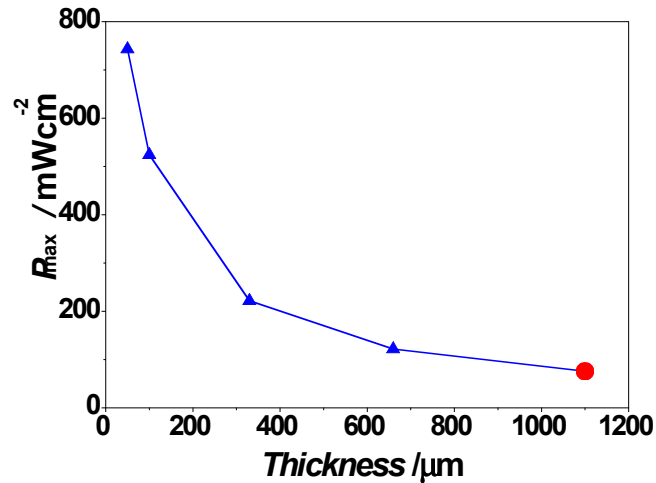


Figure 16. Calculated values of the monolithic cell maximum power density (P_{max}) for thinner configurations based on the measured data: (●) measured; (▲) calculated.

Since the development of the monolithic concept emerged during the implementation of the project as an additional idea, which should be first proved, it was not technologically optimized. A step towards the preparation of a full monolithic cell was the development of BCY15-based cathode (BCY15-LSCF48 composite). Due to the application of a single material, the already developed procedures, as well as other technological approaches can be easily introduced for the preparation of full monolithic dual membrane fuel cell of the type: BCY15 + LSCF48 / dense BCY15 / porous BCY15 / dense BCY15 / BCY15 + Ni. A new technological procedure applying tape casting and co-sintering for preparation of thinner cells is under development.

The results presented above focused on the monolithic new development of the IDEAL-Cell concept. These are results obtained lately. During the course of the project, improvements of the original concept were achieved regularly, step by step, playing on the quality of the material, control of shaping and microstructure, with the help of modelling. Figure 17 below shows clearly the dynamic of this improvement.

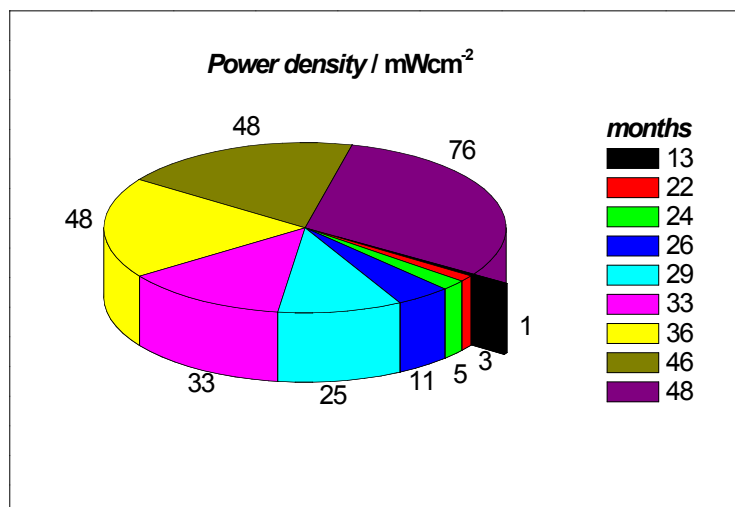


Figure 17. Power density (700 °C) progress of the dual membrane shaping via ceramic processes during the implementation of the project

IDEAL-Cells were also obtained by plasma spraying (figure 18). Layers were there much thinner, but microcracking was visible, and some chemical heterogeneities were observed. Nevertheless, as seen below with results from traditional ceramic shaping (table 3), results for plasma sprayed cells are very promising, especially because plasma spraying is a technique highly industrialisable.

Table 3. Measured maximum power density P_{max} of dual membrane cells produced by different technological approaches.

Technology	Plasma Spraying		Ceramic technology		Monolithic cold pressed; Pt electrodes	
Cell	Full Cell	ECMA	Full Cell	ECMA	Full Cell	ECMA
Thickness / μm	180	130	500	180	1100	1050
P_{max} / 600 °C	39	-	-	-	45	53
P_{max} / 700 °C	75	130	48	160	76	92
P_{max} / 750 °C	-	-	-	-	88	-
P_{max} / 800 °C	132	-	-	-	101	-

ECMA : Electrolytes and Central Membrane Assembly.

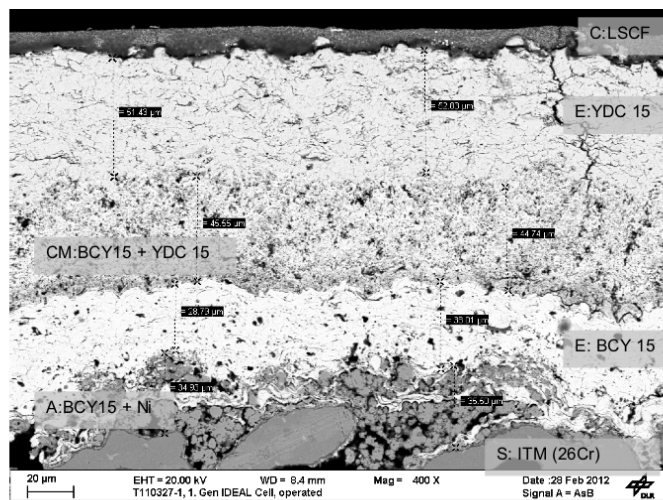


Figure 18. Plasma sprayed IDEAL-Cell; C: cathode; E: electrolyte; CM: central membrane; A: anode; S: metallic substrate.

Comparison of the monolithic IDEAL-Cell with SOFCs and PCFCs

The three concepts were tested on electrolyte supported button cells prepared by cold pressing and sintering. Pt electrodes were deposited by slurry coating following the procedure of the Pt ink producer. Since the kernel of the concepts is the mechanism of ion conductivity, the application of Pt electrodes eliminates the influence of the electrodes quality on the cell performance. In addition, it is to be emphasized that very thin cells were not looked for, for robustness reasons and also for obtaining stronger impedance signals easier to decipher. Therefore, cell in the millimetre range were fabricated. The following button cell model configurations were tested:

- Pt / YDC15 / Pt (SOFC) – electrolyte thickness 1.1 mm and 1.7 mm;
- Pt / BCY15 / Pt (PCFC) – electrolyte thickness 1.1 mm (1st generation) and 0.66 mm (2nd generation);
- Pt / dense BCY15 / porous BCY15 / dense BCY15 / Pt (monolithic dual membrane cell) – electrolyte thickness 1.0 mm and 1.9 mm (1st generation) and 1.1 mm (2nd generation).

Experimental results for the PCFC and SOFC button cells behaviour at operating conditions are presented in figures 19 and 20.

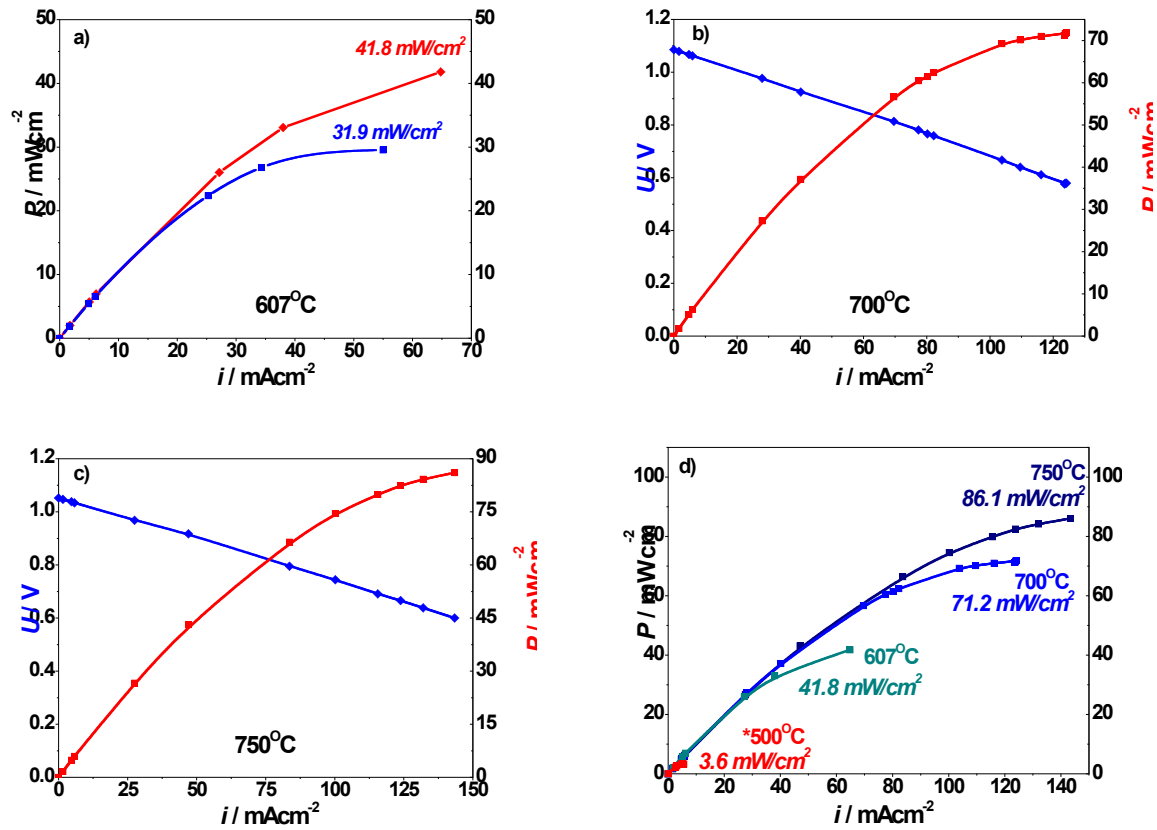


Figure 19. Current density/voltage curves and power density of PCFC (2nd generation – thickness 0,66 mm) as a function of the temperature at a constant gas flow (90% wet hydrogen and 90% oxygen). In (a) curve (■) is for 20% wet hydrogen and 20% oxygen.

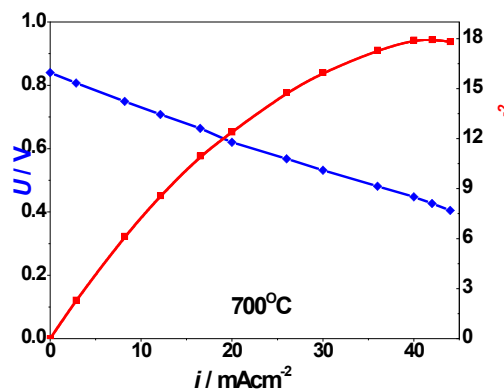


Figure 20. Current density/voltage and power density curves of SOFC (thickness = 1.1 mm).

A comparison of the 3 fuel cell concepts performance is given in figure 21 and table 3. The SOFC sample is "out of the competition" for temperatures about 700 °C. It is interesting to note that although the thickness of the monolithic cell (2nd generation) is about 40% larger than that of the PCFC, its performance is even better. Similar result was obtained from the tests of the first generation ECMA cells, reported in year 3. This improved performance of the monolithic cell is additional confirmation of the hypothesis for improved operation due to the formation of polarized hyper-liquid film in the CM and good demo-realization of the new approach in the frames of this project.

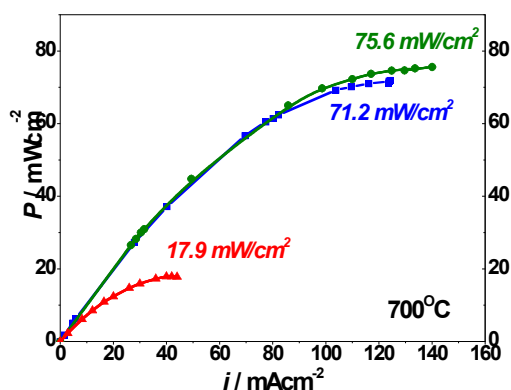


Figure 21. Power density of: SOFC ($\blacktriangle$); PCFC ($\blacksquare$); monolithic dual membrane FC ($\bullet$) at 700 °C and constant gas flow (wet $H_2 / O_2 = 90\% / 90\%$).

Table 3. Maximum power density $P_{max} / mW cm^{-2}$ measured on model cells at different temperatures: monolithic (1st and 2nd generation), PCFC (1st and 2nd generation) and SOFC.

	SOFC		PCFC		Monolithic dual membrane		
			1 st gen.	2 nd gen.	1 st gen.		2 nd gen.
Thickness / mm	1.7	1.1	1.1	0.66	1.9	1.0	1.1
600 °C	1.0	3.0	8.0	42	12	21	45
700 °C	14	18	25	71	33	48	76
750 °C	-	-	-	86	-	-	89
800 °C	-	-	-	-	-	-	101

Therefore, for cells fabricated via ceramic processes, it is seen that at all the temperatures tested and for comparable large thicknesses, monolithic IDEAL-Cell performs better than both PCFCs and SOFCs. Again, this has to be put in perspective of the respective maturity of the three configurations (50 years for SOFCs, 25 years for PCFCs, and 2 years for IDEAL-Cell). A complete technological benchmarking study has been carried out (Deliverable 6.4) that tackle these different aspects, including comparison of performances versus maturity.

Reversibility of operation for the monolithic concept

During the implementation of project and especially after the proof of the concept a niche for new activities in the direction of optimization emerged. Some of them (gases and water vapor permeability studies) were additionally included in the work-plan. Others were realized without introduction in the tasks activities, or replaced planned studies which, on the background of the quickly accumulating new knowledge and ideas, were evaluated as less effective.

The kernel of the concept was the CM and efforts were concentrated for deeper insight into the occurring phenomena. A combination of morphological, electrochemical, thermodynamic, kinetic approaches was applied. New experimental techniques were introduced, developed and improved for experimental confirmation of some hypotheses: gases permeability studies, complex permittivity spectroscopy of wet CM, impedance spectroscopy in extended low frequency range (down to 1 mHz) during cell operation. The combination of those advanced approaches brought to the discovery of new phenomenon – formation under external electrical field of self-organized dipole micelle structure in the adsorbed quasi-water based film at the pore surface of the proton conducting phase in the membrane. A hypothesis for enhanced water splitting in the CM, i.e. for better performance of the design as electrolyser, was also introduced. For its confirmation, a specialized experiment was performed in which the cell was forced to behave periodically as fuel cell and as electrolyser changing the operation mode. Under cathodic current the cell works as fuel cell, filling the pores of the central membrane with the produced water. Under anodic

current, the water from the pores should split to hydrogen and oxide ions, propagating respectively through the hydrogen and oxygen compartments. The obtained results are presented in figure 22. They show good reversibility without application of a special catalyst or water vapour pressure for enhancement of the water splitting. The electrolyser mode of operation is characterized with lower overvoltage and thus with lower internal resistance.

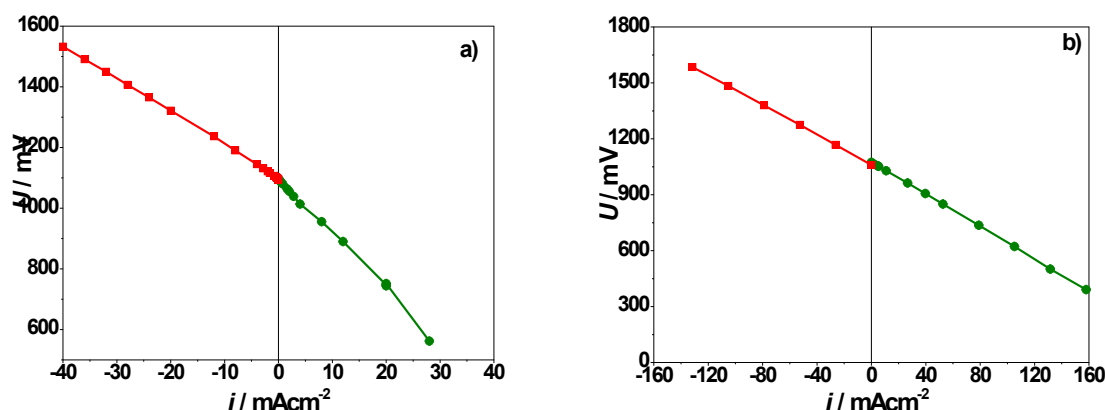


Figure 22. Current density/voltage curves of monolithic dual membrane cell in electrolyzer (■) and in fuel cell (●) operation mode: (a) 1st generation cell (1.9 mm thick); (b) 2nd generation cell (1.1 mm thick).

The better performance of the monolithic dual membrane fuel cell in comparison with the PCFC brings to some conclusions, which concern the implementation of this project, as well as future activities in related directions. The results can be regarded as a strong evidence for the advantages of the innovative dual membrane concept and its monolithic design developed in the frames of this project.

The kernel of the monolithic concept is the proton conducting BCY15 and its unique properties, related to its high activity. This activity brings to lower chemical stability towards water vapour and acidic gases. However, the reactivity of barium cerates towards water vapour decreases with the increase of the temperature. The performed in this project DTA studies confirmed the stability of the material towards water vapour at 600 °C. For commercialization of the design and of the monolithic approach new materials with good mixed conductivity and higher stability should be developed. During the implementation of the project ideas for realization of this goal were generated and some of them realised – development of BCY15 / YDC15 composites with different ratio of the two components, synthesis of In doped barium cerate. The first results confirm higher chemical stability.

The good performance of the monolithic construction opens a new niche for the development of dual membrane-based configurations. The advantages of the design come from the registered high mixed proton and oxide ion conductivity. This property is regarded for a first time as a positive. Thus in addition to the chemical stabilization of BCY15, a new pathway for development of materials with mixed ionic conductivity is opened. The optimization of the cell geometry is another possibility for improved operation. A very promising direction for further development is the application of the dual membrane cell in both fuel cell and electrolyzer mode in a single reversible device. The formation of polarized semi-liquid film in the pores of the CM needs deeper fundamental investigation for understanding the improved electrochemical behaviour of the system in electrolyser mode.

D – The potential impact

Introduction

As demonstrated above, IDEAL-Cell has attained successfully its major objectives. The concept has been proved, the performances have increased by two orders of magnitude in the course of the last two years to

reach a level potentially better than that of other high temperature fuel cell configurations. Electrode and electrolyte materials have been strongly improved, new mechanisms have been discovered, a full theoretical description of the cell has been carefully established and validated on the basis of our experimental results, the most up-to-date experimental and theoretical techniques have been used (TEM/STEM, SIMS, 3D-microtomography with synchrotron radiation, 3-D mathematical morphology reconstruction, CFD, prediction of effective properties, differential impedance spectroscopy,...) as a support for shaping the cell and understanding its behaviour. All these approaches have been pushed towards their limits, and the accumulated knowledge, technological skill and sophistication will serve as a solid and sound background from which a scientific and industrial community larger than that of fuel cell will be able to develop new ideas, new concepts, new formalisms. The success of IDEAL-Cell will lead to impacts that are expected in three domains: technical, economical and environmental, societal; the following sections will give a quick overview of those aspects, which are much more widely described in a specific project dissemination brochure (deliverable D6.2).

Technical expected impacts

As a major technical impact, IDEAL-Cell has led to a ***new innovative concept***, in which hydrogen, oxygen and water are located in separate compartments. The formation of water neither occurs at the cathode nor at the anode, as it is the case in respectively PCFCs and SOFCs. This concept has very important technological consequences, *i.e.* there is no need for a gas counter-flow to sweep the water away from the catalytic sites in the electrodes and pressure can be applied easily on both anodic and cathodic compartments to increase the overall efficiency.

This ***new innovative concept is competitive*** for the following reasons: 1/ since fuel is not diluted, the concept leads to a drastic increase of the fuel efficiency, 2/ a full optimization of the catalytic properties of the electrode is now possible (the electrodes have only a single function to fulfil, since they do not have to compromise with the presence of water), 3/ since there is no water at electrodes, there is no need for sophisticated interconnects, 4/ it allows for a better pre-heating of gas (no counter-flow, no dilution), 5/ the high quality heat carried by the pure high temperature water created in the central membrane is easily transferable to a heat exchange system or to a reforming unit, with no need for a purification stage.

Our rough estimation is that the fuel efficiency should be increased by a factor of 2 (from 40% to 80%), and the electrical efficiency by a factor of 1.5 (from 50% to 75%). Additional and significant increases in total efficiency are linked to the more efficient pre-heating of gas, recovering of heat from pure hot water and utilization of this pure water in a reforming system without any purification unit. We also proved that the concept is also able to operate efficiently as a high temperature electrolyser, in which by essence hydrogen and oxygen appear automatically in 2 different chambers, which is a key advantage compared to existing SOEC technologies in which hydrogen is produced on the water side. Furthermore, thanks to its high symmetry in its monolithic version, IDEAL-Cell itself shows total reversibility, and can alternatively operate as a fuel cell then as an electrolyser, which may be an essential advantage in many potential applications, *i.e.* those linked to renewable and intermittent energy sources.

IDEAL-Cell design is also well suited for ***scaling-up in view of energy intensive applications***: since the 3 compartments are independent, that no sophisticated difficult-to-form interconnects protective layers are needed, that there is no "open" compartment and no counter-flow of gas, IDEAL-Cell concept will give rise to new, more compact and modular stack designs easy to scale-up than existing technologies. In that sense, our ability to shape IDEAL-Cell via plasma spraying was an essential asset for further industrial development.

The advances associated with IDEAL-Cell are in phase with and reflect well the strategic objectives of the FCH JU calls for acceleration FC technologies in an integrated RTD program, which requires multinational European approach. Although based on a French patent (with additional international extensions), the initial IDEAL-Cell concept was successfully proven and developed by a selected European team, with important initial accumulated multidisciplinary knowledge (electrochemistry, solid state chemistry, electroceramics, semiconductors technology, thermodynamics, chemical engineering,

metallurgy, mathematical morphology, modeling, impedance spectroscopy, non-electrochemical testing /including different heavy characterization techniques/, nanotechnologies, inorganic chemistry, benchmarking etc.). Thus, the total of the Consortium's initial activities, expertise, overall resources and synergy overcame the resources on any single European country. National activities on fuel cells, though significant, do not offer all the required resources (scientific and technical expertises, market penetration capabilities, global strategy, financial resources...), and are directly dependant on each Gross Domestic Product, which can lead to very unbalanced development and economy stability even in Europe. IDEAL-Cell concept is a living example of an idea that could not take off at a national level, and that has needed an effort at the European level to get started.

Today, to develop further IDEAL-Cell necessitates the need for an integrated European approach. In addition to the academic experts, applied science engineers, the involvement and cooperation with stakeholders from the industry is needed. The European approach can overcome the high market entry barriers and facilitate the development of technologies for pre-industrial products. IDEAL-Cell is now in what the community calls "the Death Valley", which means that IDEAL-Cell has passed the proof of concept level, has significantly improved its performances, which level in spite of a demonstrated strong dynamic for improvement is not still high enough to attract an industrial developer for a marketable development. Owing to its clear technological advances compared to existing technologies, even if there are still lots of research activities to be carried out, which the fully operational IDEAL-Cell team is ready to get involved in, we strongly believe that IDEAL-Cell should attract industrials and will impact very positively the European fuel cell community, enabling new designs for stacks, which can be used in the next generation of fuel cells.

Economical and environmental expected impacts

This cannot be really separated from the precedent point since any increase of a system's efficiency has a positive counterpart on our environment. To ensure an effective action against climate change and GHG effects, and to ensure energy security and stable economic conditions, the European strategy for sustainable, competitive and secure energy states that the 21st century energy landscape should be one in which the world's economic region are dependant on each other. Amongst the lines of action that have been defined by the EC to fulfil its strategy for energy, several are precisely addressed by the IDEAL-Cell project, namely:

- *improve energy efficiency throughout the energy system;*
- *accelerate the penetration of renewable energy sources;*
- *diversify Europe's energy mix;*
- *enhance the competitiveness of European industry, including throughout a better involvement of SMEs.*

IDEAL-Cell will lead to a ***significant improvement of the energy efficiency***, as it is shown above, to the ***acceleration of the penetration of hydrogen as a renewable energy sources***, if produced accordingly (*i.e.* electrolysis of water via solar cells), to the ***improvement of the penetration of high temperature fuel cells on the European market***, diversifying therefore the sources of energy, to the ***enhancement of the competitiveness of European industry***, in particular with regards to Japan and USA, with the involvement of NAXAGORAS, Marion Technologies and Visimbel. IDEAL-Cell will therefore, at its own measure, play a real role in the preservation of our environment and climate.

A tremendous knowledge has accumulated inside the IDEAL-Cell Consortium, which in turn has dedicated an important effort to disseminate this knowledge towards the scientific community and the general public, as seen in the different sections and deliverables of the present reporting. This can be regarded as an important "human deliverable" which contributes to the dissemination of the European policy for moving towards a sustainable energy economy, achieving the 2020 targets and the 2050 vision for decarbonization, and placing Europe at the forefront of fuel cell technologies. Those external dissemination activities are also closely related to the European target for the development of a knowledge-based society.

Societal expected impacts

A successful IDEAL-Cell project should be able to generate societal impact through the acceleration of acceptance of hydrogen as a renewable source of energy or energy storage vector, through the education of the general public via the dissemination of the IDEAL-Cell acquired knowledge, and through the dissemination of scientific and technical results towards the Fuel Cell community.

Real time dissemination of information and accurate data regarding hydrogen and fuel cells is important to help improving investment decision in this segment. The development of hydrogen systems needs high quality resource information, key economic and technical partners and educated users of the data that are able to speed up the penetration of hydrogen and fuel cells systems. The diffusion of data and knowledge is incredibly enhanced if it can rely on relays in different countries, and an international consortium is of prime importance in that respect. A particular attention has been paid to these aspects by the consortium, though WP6, which is fully dedicated to the dissemination of knowledge through its publication strategy, internal training, organization of workshops and edition of dissemination deliverables.

The hydrogen economy has something remarkable in that it will remodel the energy landscape: hydrogen is available everywhere, and energy production will be less and less linked to the regions homing the traditional hydrocarbon resources. In particular, hydrogen will represent an historical revolution for many non-prosperous countries lacking hydrocarbon resources or hydroelectric capabilities, not to say nuclear plants, but having coastlines or water resources. The EC has an important role to play in that prospect, and any advance in the high temperature Fuel Cell technology will bring a new brick to the construction of a more stable world. The IDEAL-Cell partners want to believe that, at their scale, their motivated work in the frame of the project will bring some momentum to the general impact of the hydrogen economy development, in particular toward the less prosperous countries.