

**DEVELOPMENT OF INDUSTRIALLY RELEVANT M.C.F.C. STACKS
(D I R E M)**

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CONTENTS

| | |
|--|----------------|
| ABSTRACT | page 4 |
| 1. OBJECTIVES | page 6 |
| 2. TECHNICAL DESCRIPTION OF THE WORK | page 8 |
| 2.1 Stack design, manufacturing and testing | page 8 |
| 2.2 Development of new materials and components | page 15 |
| 2.3 Cost evaluation | page 22 |
| 3. RESULTS AND CONCLUSIONS | page 23 |

ABSTRACT

The general objective stated for this project was the development of industrially relevant MCFC stacks to give a contribution towards commercialisation phase of power plant based on Molten Carbonate Fuel Cell. Starting from the analysis of the critical problems experienced by the Contractors in developing m.c.f.c technology in previous and parallel projects, and after having defined improvements needed for materials and stack design, aimed to reduce costs and to improve performances, the activities of the projects were focused on the following areas:

- development of new stack design solutions and improved stack components, aimed to extend stack life and to reduce stack costs, followed by manufacturing, assembling and testing of 3 m.c.f.c. stacks incorporating the improved materials and components
- basic researches aimed to develop new cathode and manifold seal materials, and to improve fuel processing and impurity tolerability in m.c.f.c power plants; experimental validation of these new materials and components, through m.c.f.c. single cell tests and dedicated test rigs experiments
- cost analysis for m.c.f.c stacks and power plants components

Very important results have been obtained by developing the project activities. About the modification adopted for cell configuration and for stack design, and tested both in single cell and full-area stacks, significant improvements have been obtained, also in terms of lifetime and performances. In particular:

- a higher matrix thickness has been proposed and tested in single cells and then in STAD-1 and STAD-3 stacks; the effectiveness of higher matrix thickness adopted was shown by all tests.
- a new shape for stack cells has been studied and tested. The advantages expected from the new cell geometry adopted for the final stack STAD-3 (having rectangular cell shape, instead of the square cells used in all previous stacks) have been confirmed by the stack test results.
- a new approach for electrolyte migration control has also been studied and experienced in stack STAD-1, that showed the effectiveness of the new design adopted. From these test we obtained key data useful for designing and properly sizing special device for future market- entry stacks.

A significant effort has been devoted within the project also to improve performances and characteristics of materials for cell and stack components:

- A new material for manifold sealing has been identified as possible substitute for the state-of-the-art gaskets; this material has been fully characterised and tested, both in test rigs and the sub-scale scale stack STAD-2.
- innovative porous cathodes of lithium cobaltite and doped lithium cobaltite has been fabricated and tested in m.c.f.c. single cells; the cathodes showed good performances.
- in order to solve the problems of nickel precipitation and consequent matrix shorting in long term tests, lithium ferrite porous layers have been developed and tested in single cell tests, showing same performances as cells with standard NiO cathodes
- a significant experience in selection, characterisation and testing a wide range of operational parameters of reforming catalysts for steam reforming reactors have been developed.
- experience in running long-term single cell tests (over 10.000 hours of continuous operation) as far as diagnostic tests on m.c.f.c single cell has been achieved

A simplification and optimisation of assembly procedures for the full-area stack has also been obtained. In fact some of the modification introduced into the design of the full-area stack STAD-3 were also aimed to simplify the assembly operation and to reduce the assembly time.

Very important results have been also obtained from the carrying out of the stack tests:

- the Guadalix test plant showed, by running STAD-3 stack conditioning and steady-state tests, a good flexibility and reliability. After having hosted the 100 kW stack of the MISDAT Project and the 11 kW stack STAD-3 of the DIREM project, it is foreseen that it will host, after the requested modifications, the conditioning phase for next "Series 500" stacks that will be constructed by the Italian -Spanish consortium.
- new diagnostic tests have been performed and set-up during the operation time of all stacks of the project, showing good effectiveness and reliability in monitoring stack performances and status.

The analysis concerning the MCFC power plants configuration and base unit sizing, based also on the results of full area stack tests, takes into account and gave rise to the following considerations and results:

- Power generation market, as a consequence of the deregulation process, is expected to shift away from large central power plants to smaller, more distributed ones;

- Small additions to the grid better meet local needs, including cogeneration, with lower risks and capital investments than very large plants;
- The well-known fuel cell modularity permits to easily multiply the power of the selected base unit thus allowing to cover the upper part of the expected market with several standard units suitably arranged.
- The capacity of fuel cells of maintaining good efficiencies also at part load allows operation up to about 40% of the rated power.

On these basis, it has been identified a rated power in the class of 500 kW which is expected to allow efficient operation in a wide range of power from about 200 kW to several MW (several units in parallel). Therefore this will be the size of the planned first-of-the-kind unit which will be constituted by two modules 250 kW each based on the original configuration "TWINSTACK[®]".

1. OBJECTIVES of THE PROJECT

The general objective stated for this project was the development of industrially relevant MCFC stacks to give a contribution towards commercialisation phase of power plant based on Molten Carbonate Fuel Cell. The starting point has been the evidence that the expected cost and performances of stacks developed with present technology are not yet suitable to meet commercial needs. So, profiting of direct expertise coming from past and ongoing projects as well as from USA and Japan developers' advances, a new crossed approach system-to-stack and stack-to-system which is expected to lead to a more effective solution has been started.

According to our starting concept, already pursued also in other projects, an effective way to gain competitiveness with MCFC systems is to develop industrially relevant stacks as much standard as possible, giving at the same time the opportunity for a strong integration with the Balance of Plant.

By this way, in fact, the same stacks, without specific tailored solutions will be suitable for use in MCFC power plants feed with various fuels thus enlarging the number of possible applications both from the plant type and from the plant size (thanks to modularity) point of view.

Such approach should lead to a stronger cost reduction, a better reliability and an easier maintenance: all these advantages are expected to give a contribution towards MCFC commercialisation phase.

According to these thoughts, the initial main goals of Direm project were defined as follows:

| | |
|---------------------|--|
| Size (Cell area) | 0.75 m ² |
| Power density: | 160 mW/cm ² |
| Fuel cell pressure: | 3.5 atm |
| Decay rate | 2 (%mV/1000 h) |
| Lifetime | 20000 h |
| Cost | 3000-4000 \$/kW (referred to the subsequent "first series" stacks) |

The availability of a stack design ready for starting industrialisation phase, based on experimentally tested solutions, would allow to define industrial needs in terms of tools and raw materials and to permit a better determination of the expected cost decreasing with the production volume increasing.

The achievement of such a target and the expected opportunity of diffused demonstration actions to validate in the medium term the results, should allow to speed-up the entry into a market which, for the next 10 years and for different applications, is expected to reach, in Europe, about 15.000 MW (for all technologies).

Many companies in the US, Japan and countries in Europe such as Germany, Italy, Spain and the Netherlands are investing heavily in the development of fuel cell technology and a number of other companies are indirectly involved as suppliers or vendors. In case of technical and commercial success, economic benefits can be forecast for suppliers of raw materials, semi-manufactured components, manufacturing equipment and control tools (often SME), for MCFC stack and BOP component developers and manufacturers (in general Companies involved in traditional Power Plant production), and for End Users which could firstly profit of environmental and modularity features of FC power plants considering that in the recent years, the benefits connected to the environmental impact have been under evaluation from the economical point of view as a "premium" per kg of reduction of the polluting agents (e.g. 0.005-0.01 \$/kg for CO₂; 0.4 \$/kg for SO_x; 1.5 \$/kg for NO_x).

In addition a better understanding of the customers needs (utilities, industries, etc.) should result in a revision of the design criteria presently adopted for the stack to render them more consistent with the users' needs.

Also the efficient utilisation of the waste heat, the potential capability for multifuel operation and the control flexibility are aspects of the fuel cell technology which need to be exploited and set off to obtain a better appreciation from the users and a more effective market penetration.

The environmental benefits of the use of fuel cells instead of other forms of power generation are well known. Fuel cells have negligible emissions of all pollutants at point of use, where most of them are due to the fuel processing system. Over a full fuel cycle the benefits are strongly dependent on what fuel and processing system is used. In case of use of hydrogen, of course, completely clean exhaust come out of the plant but, as fuel cell systems are much more efficient than competitors power generation devices, also with fossil fuels the emissions of CO₂ per unit of energy produced is significantly smaller. In addition m.c.f.c. offers the unique opportunity of an active management of CO₂.

Thus, even in the case of use of fuel cells in urban centres, partially replacing the larger power generating capacity outside cities, urban emissions will not increase and overall emissions will be strongly reduced.

The objective of the project aiming at developing industrially relevant stacks by using equipment and expertise from different European partners has a clear beneficial effect on economic and social cohesion of the regions from where the partners originate. The possible fallout of the project should generate direct and indirect environmental and social (e.g. employment) benefits in many European Countries.

2 TECHNICAL DESCRIPTION OF THE WORK

Starting from the analysis of the critical problems experienced by the Contractors in developing m.c.f.c technology in previous and parallel projects, and after having defined improvements needed for materials and stack design, aimed to reduce costs and to improve performances, the activities of the projects were focused on the following areas:

- development of new stack design solutions and improved stack components, aimed to extend stack life and to reduce stack costs, followed by manufacturing, assembling and testing on 3 m.c.f.c. stacks incorporating the improved materials and components
- basic researches aimed to develop new cathode and manifold seal materials, and to improve fuel processing and impurity tolerability in m.c.f.c power plants; experimental validation of these new materials and components, through m.c.f.c. single cell tests and dedicated test rigs experiments
- cost analysis for m.c.f.c stacks and power plants components as described hereafter.

2.1 - STACK DESIGN, MANUFACTURING AND TESTING

Three stacks were designed, constructed and tested, with the aim to test and to validate the new materials and the new design approach developed within the project.

The first stack is the so called STAD-1 stack (14 cells, 0,1 sq.meters cell area) that incorporated a new solution for the electrolyte migration control; the objective of the sub-scale STAD-2 stack (10 cells, 100 sq. cm. cell area) was to test the behaviour of new manifold seal material developed within the project; the full area final stack STAD-3 (15 cells, rectangular cell shape, cell area 0,8125 sq.meters.) was aimed to validate the new rectangular cell shape and other design improvements, as described in the following pages.

2.1.1 - INTERMEDIATE STACK STAD-1

This stack (14 cells, cell area 0,1 sq.meters) adopted a new electrolyte migration control arrangement, and a thicker matrix, with respect to previous stacks, with the aim to prevent crossover phenomena. The stack was assembled at ARI facilities in Genova; the testing was performed in Milan, at ENEL Ricerca laboratories, with an ARI test stand (see on [Fig. 1](#) the picture of stack in operation at the test stand).

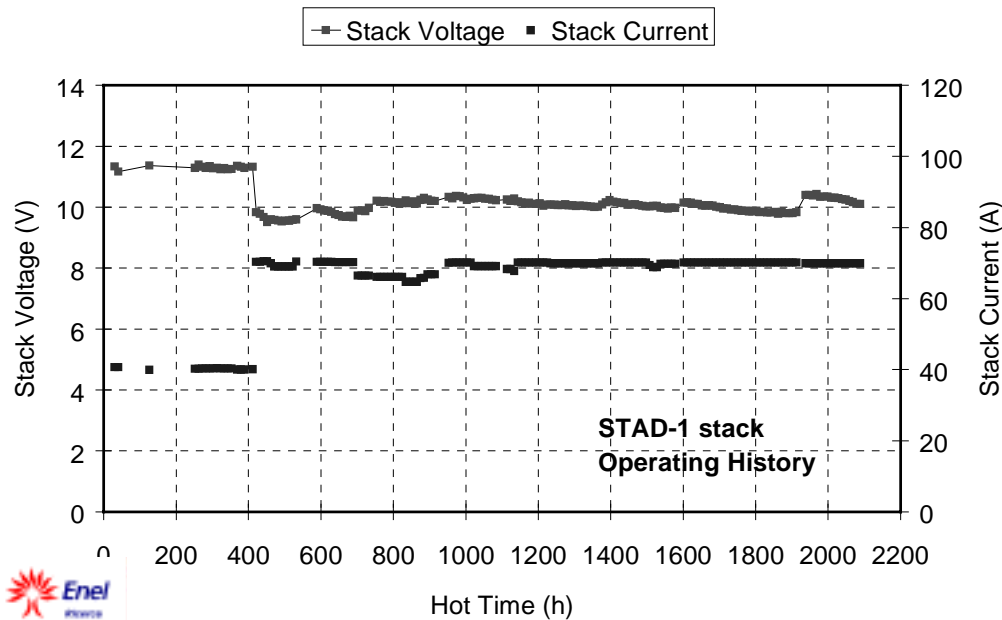


Fig. 1

The stack worked for 2100 hours as planned, according to the test program.

Apart the initial period (devoted to operations at lower current densities), usually the stack operated at 70 A, 9.8 V, with standard fuel and oxidant composition.

The stack performance history (voltage and current density versus time) is shown on [Fig. 2](#).



[Fig. 2](#)

At the expiring of the planned test duration no performance decay of the stack as a whole was detected; the test was voluntary stopped after about 2100 h..

The analysis of STAD-1 stack test results and comparison with the expected ones and with test result of previous stacks gave the following results: no gas cross-over in the cells was detected during stack life, thus showing the effectiveness of higher matrix thickness; the new electrolyte migration control device showed the capability to maintain constant performances during stack life.

Test on STAD-1 stack was chiefly a key milestone of the effort to set up solutions for the electrolyte migration control in externally manifolded stacks; the experimental results confirmed that the insertion of the designed device is an approach suitable to solve the problem. More specifically this test gave the key to design and to properly size such device for future industrial stacks.

So the identification of a solution suitable to meet a life target of 20,000 h for full-area stacks is a goal fully achieved.

2.1.2 - INTERMEDIATE SUB-SCALE STACK STAD-2

The objective of this subtask is to test the new glass material developed by BWE and ICV (see 2.2.1) as new sealing material in the real operating conditions. For this purpose a subscale stack (10 cells, cell area 150 sq.cm.) was designed and built by the Spanish partners of the Project.

The stack was assembled at Ciemat Laboratories, Madrid (E) and was tested in the same facilities; during this time, the stack was warmed up, operated, shut down restarted and finally shut-down (the shutdown was caused for problems referred to the control system, the planned life of the stack being two months). The main success is to avoid the electrolyte migration, consequently bottom cells do not show loss of electrolyte and top cells do not flood. These cells show the best performance in the stack although there is also a slight difference between centre and end cells.

After making a post-test analysis of the components hereinafter we expose some of the main conclusions.

The seal reacts with the melted electrolyte to form a material softening at a temperature higher than 650°C, but when this material appears the seal is completely adapted to the cell stack profile and the pressure applied to close the manifolds is enough to assure the sealing.

The actual guidelines of the investigation pointed to a new composition of the seal to reduce the adhesion and as a result to reduce the sealing layer.

2.1.3 FINAL STACK STAD-3

This is the final stack of the Project, therefore the design adopts several modifications, studied and developed within the Project, aimed to reduce costs (e.g. by reducing the number of stack parts, and therefore the assembly time) and to improve the performances, by modifying materials and configuration. For the Stack STAD-3 (15 cells, active area 0,8 sq. meters) the following improvements have been performed:

- ◆ a new cell configuration with a rectangular shape
- ◆ a manufacturing design of the manifold system and end-plates, suitable for the new rectangular cell configuration.
- ◆ the independent spring packages adopted in previous stacks have been eliminated. In the new configuration the current collector substitutes the function of the springs..
- ◆ the heater plates have been eliminated
- ◆ a new design for the bus bars has been developed, with the aim to reduce the number of parts, to reduce power losses on the electrical contacts and to simplify and shorten the assembly procedures.
- ◆ the design of manifold tightening system has been improved: the springs have been moved to the cold region.
- ◆ about the porous components the choices made for the STAD-1 Stack have been confirmed, in particular the use of a thicker matrix.

The squared cell configuration, adopted in all previous stacks tested by ANSALDO, has been abandoned in favour of the rectangular one; the main reason of this innovative configuration is the objective to improve the ΔP control and temperature distribution on the cell planes. Inside the cell a new important modification has been introduced: the set spring has been modified to reduce the long time of assembling. In spite of the old solution adopted up to now (a series of waved metallic strip glued together and wrapped with another one as holder) in the new configuration only the holder is maintained and the adjacent current collector substitutes the function of the other waved metallic strips.

About the active components inside the cells, the choice of the thickness used in the STAD-1 Stack has been confirmed.



Fig. 3

Assembling activities for stack STAD-3 were performed by ARI at its assembly room in Genova (see Fig. 3), then the stack has been installed in a crate, and sent to S. Agustin de Guadalix (E) for its testing at Iberdrola test stand.

The Stad-3 stack has been tested at Guadalix test plant, that hosted previously the conditioning of 100 kW stack of the Joule-Thermie Projects. Some modifications were requested on the plant, in order to perform the test: the range of operation of the Guadalix Test Plant has gone from 30 kW÷100 kW to 10 kW÷100 kW allowing the regulation of the corresponding gas flow rates and stack power output; the initial stack conditioning temperature regulation has been improved; the stack was connected to the grid via a power DC/AC converter.

To verify the functioning of the plant before starting the stack testing, the execution of a number of blank tests has been performed; before starting the test execution a first set of cold acceptance checks has been carried out in the Guadalix Clean room on the stack, and includes visual examination, gas seal leakage, electrical checks, stack height measurements, pressure test.

Then the stack was placed in the vessel by a crane, and the final connections have been made.



Fig. 4

Finally, as shown on the pictures of Fig. 4, the dome of the vessel have been placed over the stack.

According to the test plan, the new solutions used in the stack design were tested, and on load tests were performed to verify their applicability to the next projects that will use taller stacks with the same rectangular cell shape.

The stack test started on spring 1999 after the completion of the Test Stand blank tests. The stack was maintained on load for about 2000 hrs. During August 1999 a complete cool down of the stack and the test plant depressurisation were performed. After then the stack was slowly reheated and showing no degradation in its performance. The entire duration of the test period was 6 months, ending on November 1999, when the stack was cooled down and moved from the vessel to the assembling room for the post-test checks.

Firstly some tests were devoted to compare the performances obtained from STAD-3 having rectangular cell shape with those obtained by previous stacks having square shape cells.

The main points that have been compared are: stack performance, differential pressure management, temperature distribution in the cell planes, temperature distribution along vertical axis

The comparison of performances show a slightly higher stack voltage in the rectangular-shaped cells at open circuit condition (probably due to slightly different gas composition that accounts for the different test stand and gas supply systems used); when the electric load is increased these differences became greater showing a better behaviour of the rectangular shape with respect to the square one (see figure below).

**SQUARE TO RECTANGULAR CELL SHAPE
performance**

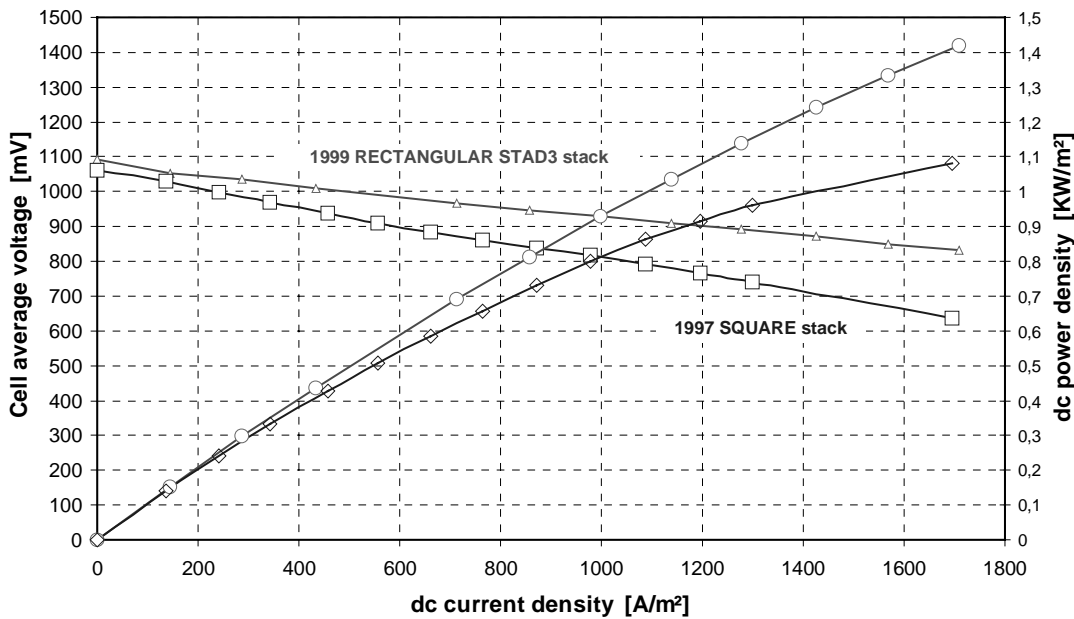


Fig. 5

The improvement obtained in the rectangular-shaped stack performance is due to the following aspects:

- Lower internal resistance, which is related to an improved stack conditioning procedure and to a good contact between stack components
- A better flow rate distribution through the stack that reduces the polarization losses.
- Not detectable crossover across matrices and therefore no performance losses were observed, thanks to thicker matrices used in last stack
- A significant reduction in cross pressure, due to the new cell geometry that improves pressure balances between the anode and cathode sides.
- A more homogeneous temperature distribution is also obtained: the temperature gradients are reduced and temperatures that could damage the stack are not reached.

To verify the applicability to the next projects of the new rectangular shaped cells, the performance of the STAD-3 stack under different operating conditions were studied by means of a number voltage vs. current characteristic curves.

The maximum load maintained at steady state conditions during the test was: current 1318 A, voltage 10.88 V, power 14.3 kW

The data shows that about the 23% overload was obtained with respect to the 11 kW nominal power of the stack calculated on the base of the previous experience on pressurised MCFC stacks.

Firstly the performance obtained in the previously tested square stack with the actual ones of the rectangular STAD3 stack were compared. As discussed above, better performances were obtained with the rectangular stack configuration from the point of view both of the stack performance, the temperature distribution in the cells and the pressure drop management.

Also the comparison with the performance obtained in the 100 kW stack previously tested on the same Guadalix Test Facility was performed. The results obtained during this test show that the performances of the new stack are better. In particular at the same current of 760 A the STAD3 stack shows an average cell

voltage of 853 mV/cell where the 100KW stack showed 663 mV/cell. An increased performance of about 28% was demonstrated using the improved new stack configuration.

On the STAD3 MCFC stack the possibility to study the stack performance using an anode richer gas composition and a higher fuel utilisation up to 75% across the stack was forecasted in the test plan. For this reason fuel utilisation tests were performed in the range 30% - 75%. The highest fuel utilisation corresponds to the stack voltage of 12.09 V, average value of 806 mV/cell, at 760 A. In terms of electrical efficiency the highest fuel utilisation corresponds to about 53.4% of the low heating value of the fuel fed to the anode inlet.

The aim of the test was also to study the stack performance using an anode richer gas composition. The gas fed to the stack simulates the gas composition coming from an improved sensible heat reforming system fuelled by natural gas and steam, working at higher temperature with respect to previously developed one. This gas composition is the same to be used in the next MCFC power plant named "Series 500".

The nominal current of about 1100 A, forecasted for the nominal operating condition of the "Series 500" power plant, was maintained at steady state condition with the above gas composition. Additional points were obtained above 1100 A and up to 1285 A without changing the fresh gas feedings to increase to fuel utilisation.

The stack performance corresponding to the nominal operating condition of the "Series 500" power plant are 1143 A at 11.07 V that is 12.65KW on a stack of 15 cells.

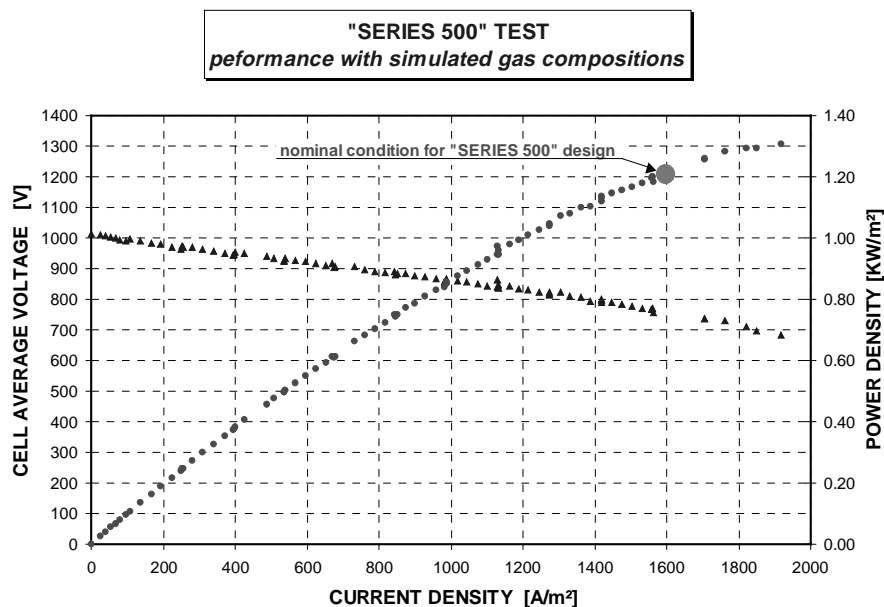


Fig. 6

As the "Series 500" power plant will contain 4 stack modules each one with 150 cells of the same area of the STAD3 stack, it means that scaling up the results of this stack about 126.5KW should be obtained on each module or 506 kW dc power should be available on the electrochemical units at nominal operating conditions, without stressing the power density.

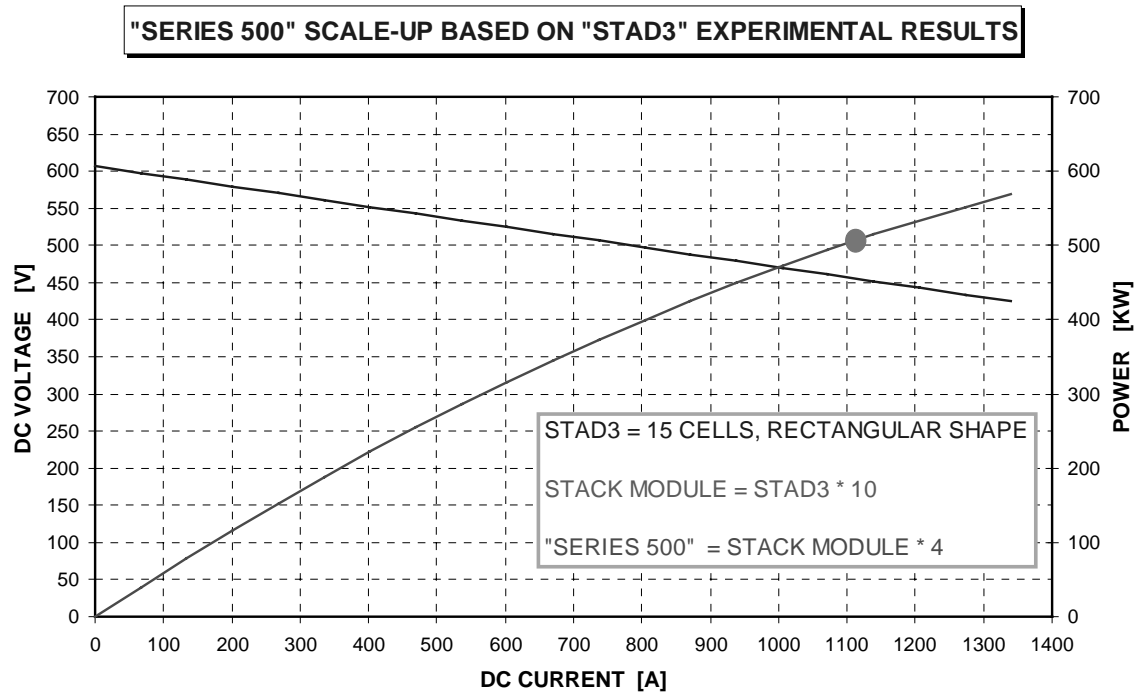


Fig. 7

These considerations are sketched on the Fig. 7, that well summarises the final result of the STAD3 stack testing: the forecasted performance for the new MCFC based power plants "Series 500" are well matched by the actual technology using the improved stack configuration defined during the DIREM project.

2.2 DEVELOPMENT OF NEW MATERIALS AND COMPONENTS

2.2.1 GAS MANIFOLDING AND RELATING SEALING IMPROVEMENT (BWE)

The aim of the work was to investigate the use of new materials and possible new configurations for the sealing of the gas manifolds when are assembled on the cell package walls.

The manifold sealing materials used in the previous stacks have been zirconia cloth and zirconia felts. The problems that present the zirconia materials and the bad results obtained with other materials tested have imposed the need of developing this task.

The sealing material must fulfil the following requirements: high resistance to electrolyte transport, high thermal resistance, good gas tightness, perfect fitting to any irregular profile, high electrical resistance and high chemical resistance against molten carbonate attack. Finally, it must be capable of working without problems during 40.000 hours, without loss of significative modification of its properties.

The initial hypothesis was that the molten carbonates attack would be minimum when the chemical activities between glass and molten electrolyte were similar.

The corrosion study carried out with Pyrex glass indicated that the attack of carbonates takes place by means of a mechanism of network dissolution instead of an ionic exchange process as initially thought.

Attackability of glasses depends strongly on their viscosity at the work temperature. So, the comparison between the different glass attackabilities must be done always in isoviscosity conditions.

Thus a glass composition with a higher silica content was proposed as the better candidate.

Different tests were carried out on such a composition to look for its capability of being tested in a stack.

The main tests were: gas tightening with and without electrolyte, enamelling alumina frames and corrosion test of the enamelled pieces, corrosion by immersion. As a consequence of the results such a glass was decided to be tested in the stack STAD-2.

The seal in the cell was subjected to the effect of carbonates attack, contraction of the components of the cell and the effect of the elongated thermal treatment at 650°C in oxidant and reducing atmospheres.

As the conclusion of this test the action was to look for a better glass composition in order to improve the behaviour versus corrosion and to try to low the glass melting temperature.

The effects of mixing the glass with a molten carbonates inert material, on the sintering and corrosion behaviour have been studied, showing a limit in the charge of inert material to be employed.

The results obtained by this way have been compared with those obtained on previous glass showing that corrosion becomes twice slower.

At temperature to which the electrolyte begins to melt, it will be a help for sealing. At 650°C, the viscosity of the softer glass will be rather low and it is expected that the attack of carbonates to the glass will take place very fast.

The conclusion of all the investigation is a very promising configuration that will allow to seal at different temperatures during the first thermal cycle and during the following thermal cycles

2.2.2 DEVELOPMENT OF LiFeO₂ CATHODES AND SINGLE CELL TESTS (ARI)

(a) Development of "Ni capture layers" materials for cathodes

For the purpose of retarding NiO precipitation into the matrix and the consequent m.c.f.c. shorting, a porous LiFe_xO_y layer has been developed.. The physico-chemical characteristics of the lithium ferrite materials layer, to be developed and tested, have also been defined; activities of powders preparations and characterisation, in cooperation with Pavia University, Dipartimento di Chimica-Fisica, aimed to obtain such cathodic structure, have also been performed; a grinding method to obtain the granulometry of the powders suitable for the fabrication of the layers has been defined. Then, starting from MCFC matrix fabrication procedure and using the above powders, we studied and developed a new procedure to obtain layers having a proper thickness.

Green tapes, suitable to obtain components for 100 sq. cm single cells, have been successfully obtained by using tape casting method.

After the characterizations of the samples (TGA and SEM analysis), an accelerated in-cell test was performed, aimed to verify performance and stability of a MCFC cell assembled with such a component (100 sq. cm. single cell; test duration 1600 hours).

This single cell showed the same performance as cells with standard NiO cathodes and a good stability in time. Figure below shows the single cell test results (Voltage versus time) and the comparison with a standard single cell.

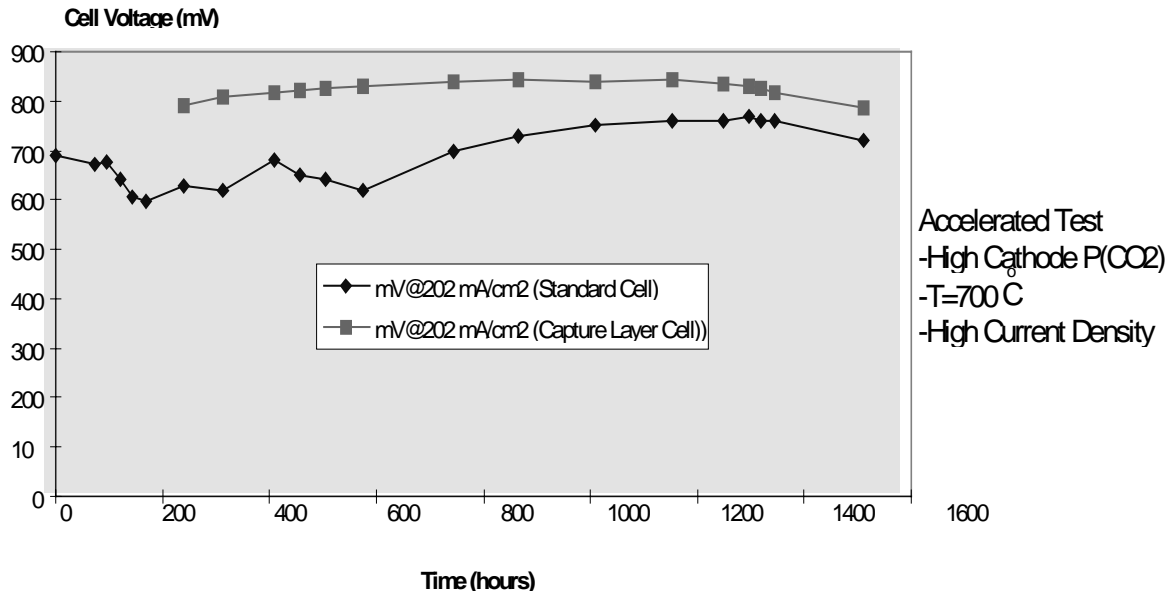


Fig. 8 - Performances of the single cell with LiFeO₂, compared with a standard single cell

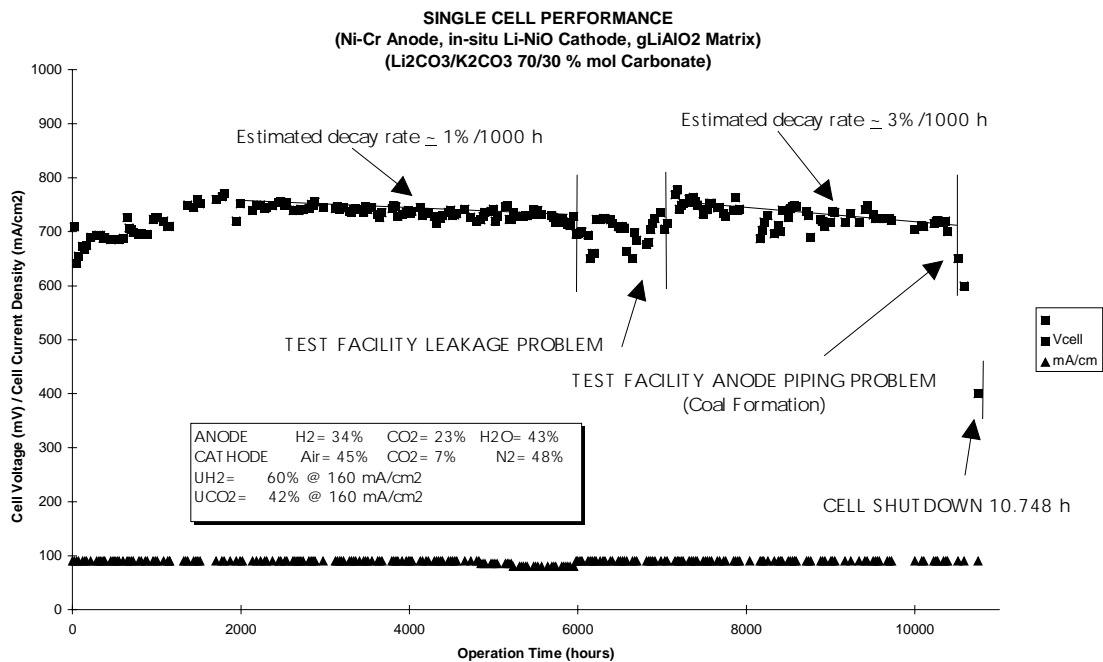


Fig. 9 - Performances of cell X70

Moreover, post test analyses confirmed the capabilities of the material to capture Ni of the cathode, dissolved in the Li/K carbonates, and reduce the precipitation of metallic Ni into the matrix; therefore the such a material results suitable for the utilization in a m.c.f.c. stack.

Single cell tests - In-cell tests have been carried out by ARI, with the aim to verify endurance and performances of porous components and cell configurations developed within the Project.

A first single cell test (same porous components and configuration; same reference gas composition as STAD-1 stack) run at ARI labs for over 10.000 hours. Fig. 9 shows the performances (Voltage versus time) of this cell, labeled X70. After 2000 hours of stabilization it is possible to estimate a first decay rate \cong 1%/1000 h (from about 2000 h to about 6.000 h).

Moreover a second single cell test (same conditions of the first test) run at ARI labs for about 5600 hours of continuous operation time.

2.2.3 DEVELOPMENT AND MANUFACTURING OF INNOVATIVE CATHODES (ENEA)

This work had the aim to develop and to manufacture porous cathodes, made of different lithium cobaltite materials, and to verify the electrochemical performances of them. Iper-stoichiometric lithium cobaltite $\text{Li}_{1.1}\text{CoO}_2$ (LICO) and Mg-doped lithium cobaltite $\text{LiMg}_{0.06}\text{CoO}_2$ (LICOA), were compared with the state of art lithiated nickel oxide (LINIO). Lithium cobaltite materials were produced by defining the synthesis of the compounds, the physical chemical characterisations, the fabrication procedure for porous electrodes, the structural characteristics, stability, electronic and electrochemical properties.

The synthesis of lithium cobaltite materials was carried out by solid state reaction, following the steps: selection of more suitable precursors (oxides, acetates, carbonates and their mixtures), thermoanalytical studies of solid state reaction, heat treatment of precursors, physical chemical characterisation, electrical/electrochemical characterisation. To introduce magnesium into the lithium cobaltite lattice MgO was used.

Thermal analysis measurements (TGA/DTA) were carried out on the single precursors and their mixtures to investigate the reaction mechanism. Then the synthesis was carried out in a furnace in air. After the synthesis, the powders were characterised by a chemical and physical point of view, with the aim to identify the true chemical composition, crystallographic structure, the absence of unreacted precursors or reaction intermediate, the particles size, the density, the specific surface area and the morphology. Our experimental results on the formation of LiCoO_2 from different precursors indicated that the synthesis take place through the reaction of lithium carbonate and cobalt oxide intermediates. The scanning electron microscopy showed different morphology of LiCoO_2 powders obtained from acetate and carbonate precursors: the acetate precursors gave finer powders, and the carbonate more homogeneous one. The BET surface area of materials from carbonate precursors is higher than those obtained from the other ones. The surface of the cobaltite materials was investigated by X-ray photoelectron spectroscopy (XPS). In addition the stability of the materials in molten carbonates at 650 °C in O_2/CO_2 atmosphere was determined together to the oxygen reduction reaction (ORR) kinetics.

The electrical conductivity increased linearly as $p\text{O}_2$ increases. The slope of the curves had nearly the same value (≈ 0.25), with positive sign, indicative for p-type semiconducting behaviour. To study the influence of doping on lithium cobaltite, the content of lithium in this compound was changed. It resulted that an increase of conductivity as a function of lithium content up to $\text{Li}_{1.35}\text{CoO}_2$ ($\sigma = 4.5 \text{ S cm}^{-1}$ at 650 °C). By doping with magnesium ($\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$) the temperature dependence of resistivity in air showed a very flat behaviour as a function of temperature and conductivity drastically increased respect to undoped stoichiometric LiCoO_2 . The doped material conductivity increased up to 5 S cm^{-1} at 650 °C.

The nickel solubility from $\text{NiO}(\text{Li})$ (around 45 ppm) was used as a reference value. The dissolution curve of LiCoO_2 in melt carbonates showed that the cobalt content increased rapidly with the time and the equilibrium solubility (6 ppm) was achieved after about 120 h.

The electrochemical stability was defined as the absence of redox phenomena in the range of operation of the cathode, excluding the oxygen reduction. The Li_xCoO_2 materials showed a quasi-reversible redox peak assigned to the reduction/oxidation of cobalt inside the compounds. The Mg-doped material, instead, did not show such peaks, indicating a very high stability.

A method for the fabrication of LiCoO_2 porous electrodes by tape casting has been developed. The following activities were carried out: definition of slurry composition, casting of small quantities of slurry by manual blade, preparation of stoichiometric and Mg-doped lithium cobaltite ($\approx 1 \text{ kg}$), tape casting of lithium cobaltite, sintering of 100x100 mm samples, physical characterisation (porosity, mean pore size) of the casted materials. After drying of tapes, some parameters were controlled: cracking of the tape during drying, tear-off from substrate, flexibility and mechanical strength of tape, thickness of the tape. The influence of the LiCoO_2 powders properties and slurry composition on the above-mentioned parameters was investigated.

Porous electrodes were casted in non-aqueous slurry with and without poreformers. The slurry formulation was studied as well as the influence of slurry components for: viscosity of slurry, tear of the green tape from support, flexibility and mechanical resistance of green tape, cracking of tape during drying, properties of sintered body.

To test the cathodic performance of the materials, electrochemical impedance spectroscopy (EIS) measurements were carried out, in a symmetric cell (electrode 3 cm^2), to investigate the porous electrode/molten carbonates interface. The long-term stability (up to 2,000 h) was determined by the change of the electrode+electrolyte resistance (R_e) and total polarisation resistance (R_p) values, as a function of time at constant conditions (temperature and gas composition).

The electrochemical behaviour of lithium cobaltite cathodes (porosity 63% and mean pore size $8 \mu\text{m}$) was tested in a single cell (up to 100 cm^2), in various operating conditions (atmosphere, temperature, and electrical load), including thermal and electrical cycling. During the experiments the cathode and anode gas compositions were changed to check for the best performances and to study the cathode kinetic. Moreover

the influence of temperature on cathode kinetic and thermal cycling were evaluated. The influence of oxygen partial pressure on polarisation characteristics is positive. It is clear a more complicated relationship between current density and pO_2 than in the case of carbon dioxide. It results that LICOA has a better performance than LICO and comparable to LINIO, if the optimal gas composition is chosen. The Mg-doped lithium cobaltite showed a very good performance compared to lithiated nickel oxide (LINIO). The best performances of LICOA were achieved by using an oxygen rich gas composition, while for LINIO it was necessary to use a less rich gas. That means that the electrochemical mechanism is very different for the two materials. In conclusion the Mg-doped lithium cobaltite (LICOA) showed, whatever the cathode gas composition, best performances respect to iper-stoichiometric lithium cobaltite (LICO). The best performances for LICOA are attained with an oxygen rich gas ($O_2/CO_2=0.81$). The best LICOA performance is comparable to that of LINIO at lower O_2/CO_2 ratio (0.44).

To compare the performance of LICOA material, the maximum electric power obtained with three different gas composition was evaluated. It resulted that LICOA has a better performance than LICO and comparable to LINIO, if the optimal gas is chosen, as shown on Fig. 10.

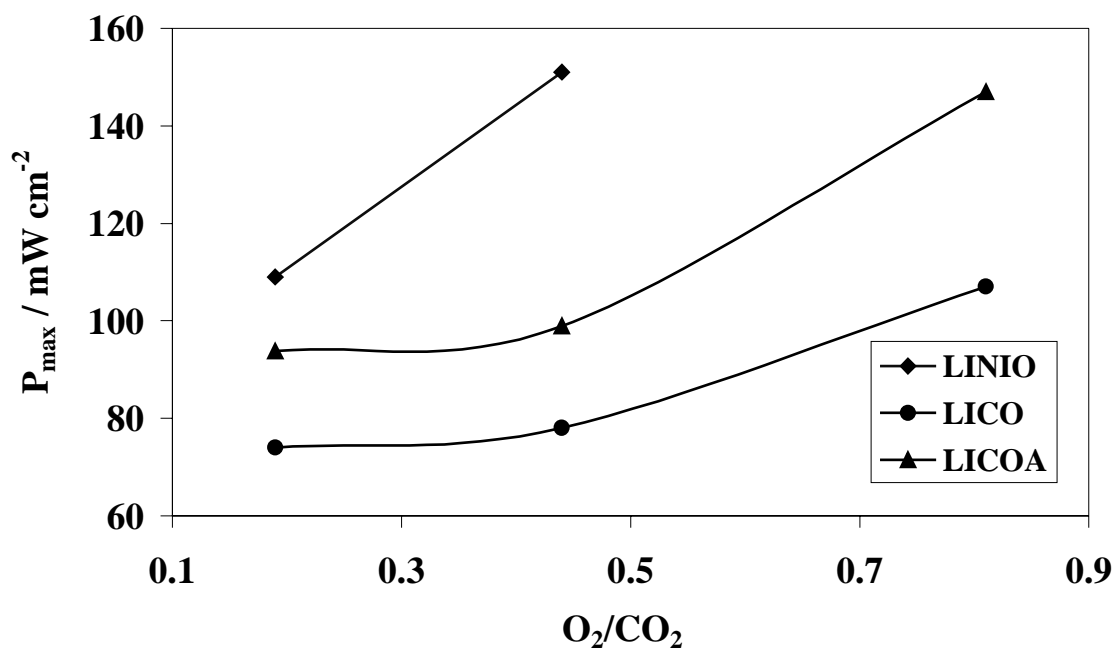


Fig. 10

2.2.4 FUEL PROCESSING AND IMPURITIES TOLERABILITY ANALYSIS (CNR-ITAE)

In the framework of the project the work of the Institute CNR-TAE was devoted to investigate the problems correlated to the management of the steam reformer and to the process gases, and concerned three main areas: i) Criteria for improving sensible heat reforming and multifuel capability; ii) Impurities accumulation and tolerability evaluation; iii) Process gas treatment.

The first task represented a critical point because of reformer performance influenced the overall plant activity. In fact, the scheme of this plant sub-module foresees a reformer, thermally integrated to the cell, supplied by a mixture of fresh natural gas and recycled anode gas, that acts as thermal vector, also. It is clear that the development of stable and well performing reformer assumed great importance in order to guarantee a constant supplying of reformed fuel, at constant composition, to the anode.

Thus, the activities started from the characterisation of the catalyst to be integrated in the reformer section. This catalyst has been characterised (XRD, B.E.T., S.E.M., Porosimetry, T.E.M., T.P.R. and A.A.) and in parallel, the procedure for its activation "in situ" has been defined as well as tests for the measurements of the catalyst activity have been carried out. The experiments allowed to investigate the influence of important operational parameters on the catalyst activity.

Particularly, it has been studied the gas hourly space velocity, the temperature that strongly influences methane conversion and gas compositions, the steam/carbon ratio that controls the equilibrium of carbon formation, and the time on stream that produces some change in morphology of the catalyst.

The CNR-TAE studied, further, the present state of art on the reformer configurations that potentially can be integrated in C.U. concept with particularly attention to the methane autothermal reforming (ATR) process. In this case, the partial oxidation is combined with the adiabatic steam reforming and the syngas composition depends by pressure and inlet $\text{H}_2\text{O}/\text{CH}_4$ and O_2/CH_4 ratios.

The ATR configuration seemed to be very promising for the considered configuration because the addition of oxygen, that exothermally reacts with the methane, allows to balance the reformer reactions for having a full thermal equilibrium.

As mentioned above, the fuel that will supply the cell anode compartment is a reformed mixture of recycled spent gas and fresh natural gas. The steam reforming represents the process selected for the production of hydrogen. The natural gas is a mixture containing several components like methane, nitrogen, carbon dioxide, heavy hydrocarbons and sulphur compound (THT, TBM). Normally, it exists a considerable risk that heavy hydrocarbons and more sulphur compounds will interact with cell or reformer components producing losses of catalytic or chemical properties.

Further, the electrolyte vapours contained in the recycled anode gas can, also, be dangerous for the reformer catalyst, as previous experiments have demonstrated.

These experiences lead us to consider additional topics concerning: i) evaluation of the interaction between MCFC components and different impurities contained in the fresh fuel, and ii) experimental investigation on the effects of some impurities on the reformer catalyst activity and evaluation of its tolerability.

Thus, a wide investigation on the effects of the above mentioned impurities on performance of anode components has been developed, as well as a set of experiments have been planned to explore how the catalytic properties of the reforming catalyst can be influenced by the presence of impurities. The sulphur appeared as the most dangerous poison for the Ni based catalysts.

The experiences done in the former tasks lead on the development of a compact module for catalytic desulfurisation of the natural gas and prereforming of heavy hydrocarbons. The development of the compact system for the clean-up of the natural gas started from the consideration that carbon dioxide, that can promote the COS formation, heavy hydrocarbons and sulphur compounds (T.H.T. and T.B.M.) are products that must be separated from feeding gas.

Then, two technical solutions have been studied to solve the problem of sulphur poisoning: i) sulphur removal by regenerable adsorbents and ii) sulphur removal by non regenerable adsorbents.

The tests demonstrated that Ni/MgO catalyst (TAE-N3) was the most active adsorbent for sulphur compounds and its activity towards prereforming of heavy hydrocarbons reached the maximum at temperature of 450 °C. Thus, this adsorbent has been selected as material for the gas clean up system and it has been characterised by TPR analyses, H_2 Chemisorption, TEM, and the mechanism of sulphur adsorption has been, also, investigated. Then, the developed system has been, successfully, tested in order to verify its effectiveness under operative conditions.

Molten carbonate fuel cells are characterised by the requirement to recovery the CO_2 produced in the anode to be recycled in the fresh cathode gas. Thus, CNR-TAE started with a research on a preliminary screening of the available technologies for the carbon dioxide extraction and the analysis of the problems arising from their integration to MCFC-CU. The theoretical feasibility and the technical reliability of different methods have been evaluated, and that based on Methyl-diethanolamine (MDEA) liquid absorption appeared to be the most appropriate for MCFC use.

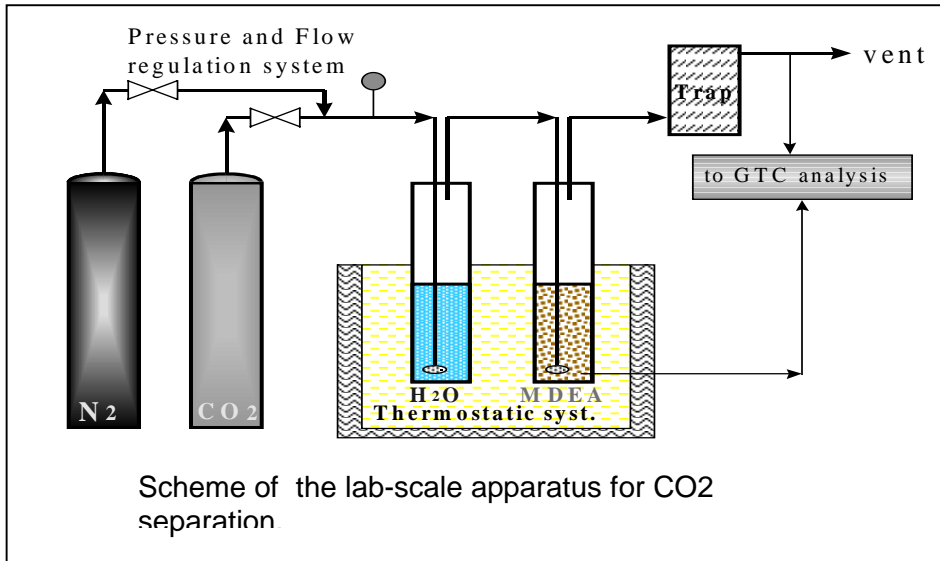


Fig. 11

The experiments showed MDEA as a system integrable in MCFC plant, even if, some aspects should be optimised in order to enhance the compactness of the plant and to reduce its complexity and energy consumption.

The last critical examined point regarded the clean up of the recycled anode gas. In fact, it has been demonstrated that anode gas contains alkali vapours that produce the deactivation of the reforming catalyst. From past experiences, it has been estimated the amount of alkali transported by the anode outlet gas for a 100 kW MCFC stack. The result, compared with the measurements of the reformer catalyst tolerance to the alkali, indicates that electrolyte vapours diffusion on the catalyst should be reduced. Then, the evaluation and selection of materials to be used as adsorbent for the clean up of the anode stream as been done. Different compounds as Al_2O_3 , SiO_2 , MgO , B_4C and BN have been selected and tested in the experimental apparatus in order to measure their effective capability to retain alkali vapours. The results evidenced as silica at high specific surface area seemed a suitable adsorbent material and the feasibility of a clean up device has been demonstrated.

2.3 COSTS EVALUATION

The costs for the stacks and for the plant still represent a challenging aspect for the MCFC technology as well as for the other FC technologies.

For this reason and also on the basis of direct experiences both at stack and system level, a new crossed approach “system-to-stack” and “stack-to-system” has been continuously pursued on the development of DIREM Project.

In this framework, the actions aimed at cost reduction have been focused on stack materials, manufacturing processes, geometry's, general arrangements consistent with the operating conditions planned for its integration in a new, simplified plant configuration.

Of course durability features and maintenance characteristics have been also considered so to be able to launch, as soon as ready, m.c.f.c. industrial development.

To this aim it has been confirmed the main technological options of using external manifolding-cross flow and external integrated reforming systems which lead to a higher level of stack standardisation.

Analyses and evaluations of the actual capability of MCFCs of becoming a commercial product, taking into account also some experienced indicators strongly affecting the costs of the stack which can be closely related to the improvement of the stack design and technology, to the learning curve and to the production volumes, have been made showing that the cost target of about 1500 E/kW planned for 2005 should be achievable. A synthesis of the results coming from such analyses is given in fig. 10(1), which shows the expected splitting of costs (plant, stack, porous components) with reference to years and volumes in the demonstration, pre-commercial and commercial phases. The values up to the year 2015 are based on market assumptions consistent with independent market analyses commissioned by the contractors to identify the earlier niches possibly giving opportunities for specific applications also with reference to the availability of various fuels.

The general trends synthesised in the figure below (expected costs for mcfc, ECU/kW, vs.time) allow to be confident about the capability of MCFCs of reaching the short-medium term targets and requirements, which are considered the base for subsequent commercialisation.

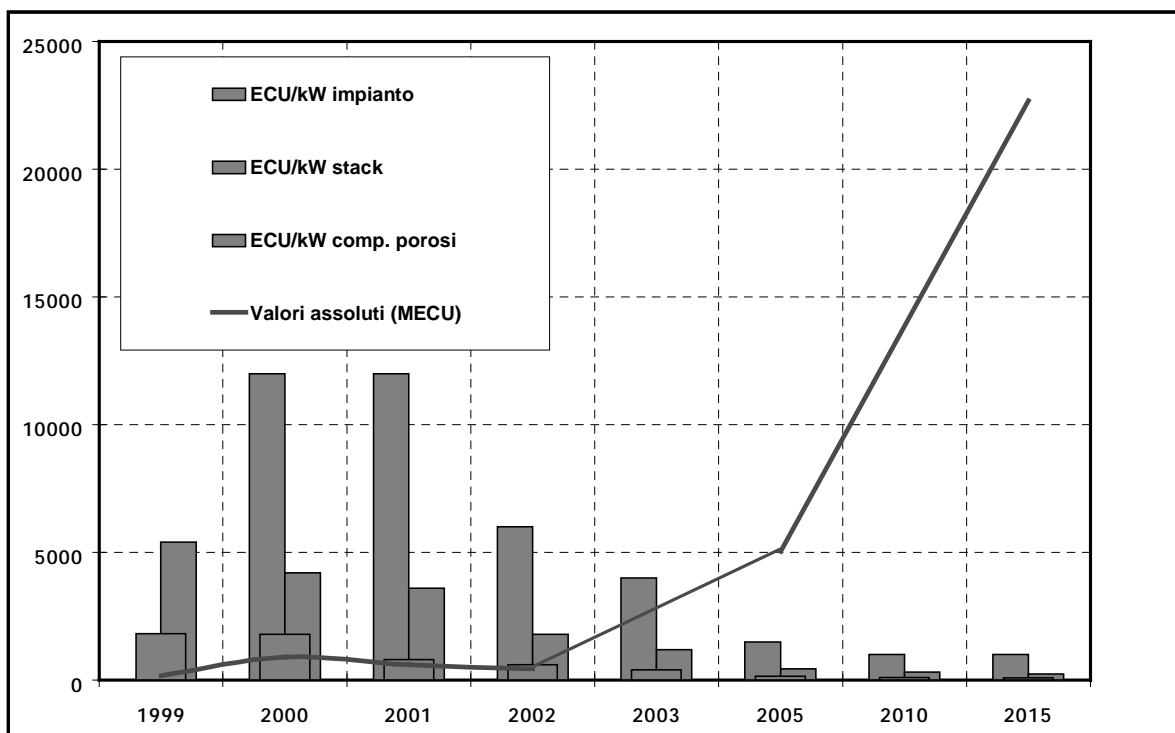


Fig. 12

3. RESULTS AND CONCLUSIONS

Very important results have been obtained within this project about the following topics of m.c.f.c. technology: (a) cell and stack design; (b) materials; (c) fabrication of stack components; (d) stack assembly; (e) stack testing; (f) power plant configuration.

About the modification adopted for cell configuration and for stack design, and tested both in single cell and full-area stacks testing, significant improvements have been obtained, also in terms of lifetime and performances. In particular:

- A higher matrix thickness has been proposed and tested; the effectiveness of higher matrix thickness, adopted in single cells and then in STAD-1 and STAD-3 stacks, was shown by all tests. The improvements due to this approach are lack of gas crossover through the matrix and increasing of cell life, without significant performance decay.

- A new shape for stack cells has been studied and tested. The advantages expected from the new cell geometry adopted for the final stack STAD-3 (having rectangular cell shape, instead of the square cells used in all previous stacks) have been confirmed by the stack test results.

In fact with the new cell configuration the pressure balances between the anode and the cathode chambers have been improved, with a significant reduction in cross pressure, and a more homogeneous distribution of temperature on the cell planes have been obtained. These results confirmed the validity of the new approach to the rectangular cell shape for full-area stacks, which is also confirmed for next "Series 500" stack.

- A new approach for electrolyte migration control has also been studied and experienced. The tests made on the intermediate stack STAD-1, having 0,1 sq. meters cell area, showed the effectiveness of the device adopted for electrolyte migration control. From these tests we obtained key data useful for designing and properly sizing such device for future market- entry stacks. By using the same design up to 20.000 hours lifetime can be reached for a full area stack (higher endurance are possible by properly increasing the size of the device).

- An improved design for the stack bus bars has been developed and then adopted for the final stack STAD-3. The same approach is also envisaged for next "Series 500" stacks.

A significant effort has been devoted within the project also to improve performances and characteristics of materials for cell and stack components:

- A new material for manifold sealing has been identified as possible substitute for the state-of-the-art gasket; this material has been fully characterised and tested, both in test rigs and the sub-scale scale intermediate stack STAD-2. The new material is promising, but not yet ready for immediate use in large stacks; further development is needed to improve the corrosion resistance and the behaviour during thermal cycling.

- innovative porous cathodes of lithium cobaltite and doped lithium cobaltite has been fabricated and tested in m.c.f.c. single cells; the cathodes showed good performances.

- in order to solve the problems of nickel precipitation and consequent matrix shorting in long term tests, lithium ferrite porous layers have been developed and tested in single cell tests, showing same performances as cells with standard NiO cathodes; moreover post-test analyses confirmed the capability of this approach in reducing Ni precipitation, and the possibility of its utilisation in a m.c.f.c. stack.

- a significant experience in selection, characterisation and testing a wide range of operational parameters of reforming catalysts for steam reforming reactors have been developed.

- experience in running long-term single cell tests (over 10.000 hours of continuous operation) as far as diagnostic tests on m.c.f.c single cell has been achieved

The fabrication of stack parts of the intermediate stack STAD-1 (14 cells, cell area 0,1 sq. meters) and of the final stack STAD-3 (15 cells having rectangular shape, cell area 0,8 sq. meters) of the project, gave rise to the following results/improvements of stack technology:

- all the stack components (both metallic and porous parts) have been manufactured by European vendors; the European vendors have been qualified for the production of full-size (0,8 sq. meters cell area) stack components.

- reliable coating processes for the metallic stack components have been set-up

- a standardisation of manufacturing processes for porous components (anodes, cathodes, and matrices) has been obtained.

A simplification and optimisation of assembly procedures for the full-area stack has also been obtained. In fact some of the modification introduced into the design of the full-area stack STAD-3 were also aimed to simplify the assembly operation and to reduce the assembly time. The reduction of assembly time and costs, as a result of the above design improvements, has also been proved.

Very important results have been also obtained from the carrying out of the stack testiness:

- the Guadalix test plant showed, by running STAD-3 stack conditioning and steady-state tests, a good flexibility and reliability. After having hosted the 100 kW stack of the MISDAT Project and the 11 kW stack STAD-3 of the DIREM project, it is foreseen that it will host, after the requested modifications, the conditioning phase for next "Series 500" stacks that will be constructed by the Italian -Spanish consortium.
- new diagnostic tests have been performed and set-up during the operation time of all stacks of the project, showing good effectiveness and reliability in monitoring stack performances and status.

The analysis concerning the MCFC power plants configuration and base unit sizing, based also on the results of full area stack tests, takes into account and gave rise to the following considerations and results:

- Power generation market, as a consequence of the deregulation process, is expected to shift away from large central power plants to smaller, more distributed ones;
- Small additions to the grid better meet local needs, including cogeneration, with lower risks and capital investments than very large plants;
- The well-known fuel cell modularity permits to easily multiply the power of the selected base unit thus allowing to cover the upper part of the expected market with several standard units suitably arranged.
- The capacity of fuel cells of maintaining good efficiencies also at part load allows operation up to about 40% of the rated power.

On these basis, it has been identified a rated power in the class of 500 kW which is expected to allow efficient operation in a wide range of power from about 200 kW to several MW (several units in parallel). Therefore this will be the size of the planned first-of-the-kind unit which will be constituted by two modules 250 kW each based on the original configuration "TWINSTACK[®]". Each stack of this module is directly derived from the STAD3 of DIREM, the only difference being the cell number in the stack (150 instead of 15). From this point of view, the results obtained on the STAD3 extrapolated to 150 cells show that a power of 500 kW is easily achievable, without stressing the power density.

(publish2)