Fuel Cells DOI: 10.1002/fuce.200800064

A Cylindrical Small Size Molten Carbonate Fuel Cell: Experimental Investigation on Materials and Improving Performance Solutions

F. Rossi[1], A. Nicolini[1]*

[1] Department of Industrial Engineering, University of Perugia, via G. Duranti n.67, 06125 Perugia, Italy

Received July 28, 2008; accepted December 03, 2008

Abstract

An original cylindrical small size molten carbonate fuel cell is presented. The cell's main peculiarity is its unique architecture in terms of both elements geometry and gases arrangements. Experimental tests on materials and system solutions were carried out on a single cell preliminary facility. Results allowed to identify optimising solutions which were applied on a new single cell facility. Further experimental tests allowed to determine the final cell configuration where sealing is enhanced and compression strain is further kept uniform along the cell surface. Final tests were carried out on a 1 kW stack comprising 15 single cells. Results suggest that the proposed cell design is a promising solution for μCHP applications because of performances, durability and construction costs.

Keywords: MCFC, Geometry Variations, Experimental Results, High Temperature, Residential Application

1 Introduction

The presented cylindrical small size MCFC (SSMCFC) is the result of multi-annual activities carried out at the Fuel Cell Laboratory of University of Perugia headquartered in Terni (Italy). SSMCFC is patented by IPASS [1], a partnership between CIRIAF (inter-university research center on physical agent pollution) and FN S.p.A. (an industrial partner). It was studied and its theoretical performances were simulated with a numerical code [1, 2]. The SSMCFC main peculiarity is the geometry of the cell elements and the arrangements for gases distribution. High benefits may be obtained by the proposed configuration. Cylindrical elements may be easily obtained by injection printing; this is a moulding technique which is conveniently used for large-scale productions because of time and cost advantages. Moreover, cylindrical configuration produces lower heat losses because of high volume regarding surface. The theoretical investigation was the object of previous publications and it is the starting point for the experimental study [2, 3]. The present paper deals with experimental tests and improvements on the identified SSMCFC. The theoretical investigation was followed by a study on new materials, treatments and procedures suitable for improving the performances of the cylindrical molten carbonate fuel cell. The investigation was carried out by manufacturing a single cell preliminary facility (SCPF) which was used as a test bench. By means of SCPF the following components were tested:

- electrolyte matrices obtained by tape casting and injection moulding formation techniques;
- cathodes and anodes obtained by tape casting formation techniques;
- new materials for electrodes mechanical support.

Results showed that binder burnout is quicker and less carbonic residues occur on matrices obtained by injection moulding. Besides, the proposed electrodes support system provides high mechanical resistance.

Preliminary test findings suggested to build an innovative cylindrical MCFC configuration which was tested by a single cell improved facility (SCIF). Experimental tests on SCIF showed that the proposed new solutions allowed to improve

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[*] *Corresponding author, nicolini.unipg@ciriaf.it*

the cell performances: sealing was enhanced and compression strain was kept more uniform along the cell surface. The original gases arrangement was attained in SCIF by stacking circular holed thin steel rings and nettings. Nettings also have the role of electrodes support system studied by SCPF. Tests were carried out to determine voltage/current characteristic under different conditions by using hydrogen as a fuel with and without steam injection into the cathodic compartment. Cell resuming performances were also verified when a temperature drop occurs. Maximum power density was evaluated under different conditions. Results allowed to design and build the cylindrical MCFC final configuration (SSMCFC).

In particular, an innovative tie system was designed and realized. Cell elements (electrodes, electrolyte and distribution plates) of the final configuration are placed into a cylindrical vessel. Sealing is further enhanced and compression strain is further kept uniform along the cell surface by the tie system and an original stacking frame. The new original system also contributes to reducing heat losses. Tests were carried out on a 1 kW stack comprising 15 single cells. Voltage/current characteristic is obtained for different working conditions using hydrogen as a fuel. Maximum power density was also evaluated. Tests were also carried out also by implementing a control and monitoring system for SSMCFC. New methods were proposed to optimise cell fabrication times and to reduce manufacturing costs: results confirm the cell design as a promising solution for μCHP applications because of performances, durability and low realisation costs.

2 The Single Cell Preliminary Facility (SCPF)

A SCPF was built (see Figures 1 and 2). SCPF allowed to test innovative materials for small size cylindrical MCFCs [1]. Besides, SCPF allowed to identify the optimum treatment procedures for MCFC elements and optimise the MCFC start-up procedure.

SCPF is constituted by:

1. a single MCFC (a nickel-oxide porous cathode, a lithium aluminate porous matrix, a nickel–chrome porous anode, gases distribution plates and electrical current manifolds) [2, 3];
2. a mechanical system for the cell stacking;
3. a heating system for the cell elements and inlet gases.

Distribution plates are steel disks. Flared holes plates are mounted between each distribution plate and the corresponding electrode. Flared holes plates are used as current manifolds. Inlets for the gases are on the distribution plates; gases pass through the flared holes and touch the electrodes. The electrodes were built by tape casting; this procedure allowed to create channels for exhaust gases which exit through the steel pipes. Seal of the gases is achieved through a matrix the dimensions of

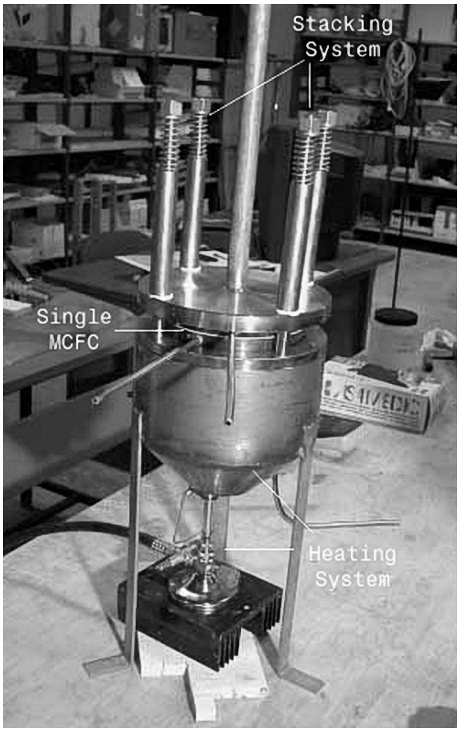

Fig. 1 The SCPF.

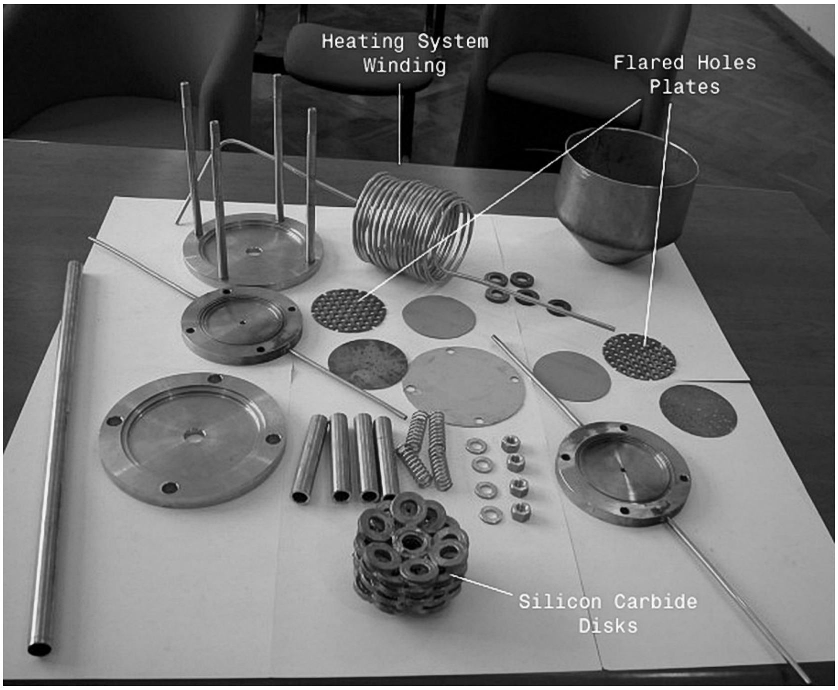

Fig. 2 The elements of SCPF.

which are greater than those of the electrodes. The frame is constituted by steel plates which keep the distributors and the single cell elements compressed by springs and steel ties.

The cell heating system is constituted by silicon carbide disks (diffuser) and a bunsen burner. The system provides the start-up procedure and the inlet gases heating. The disks enhance heat diffusion in order to reduce temperature disuniformities. The diffuser is placed into a steel box placed in the SCPF bottom side. Anodic inlet gases heating is directly fed by the burner (anode is placed in the MCFC bottom side); cathodic inlet gases heating is fed by the burner through a winding pipe. Temperature setting is regulated by an automatic system constituted by thermocouple sensors which control the burner fuel and air flow rate. The system thermal insulation was obtained by ceramic fibres the efficacy of which was verified by a measurement campaign. In particular, the insulation material superficial temperature is lower than 50 °C when the cell temperature is 650 °C.

3 Experimental Tests by SCPF

Experimental tests were carried out in order to determine the optimum treatment procedure for the cell elements (matrix binder burn-out and impregnation with carbonates, cathode oxidization and lithiation). Two matrices were tested: the first is obtained with traditional tape casting [4, 5]; the second by injection moulding. The latter displayed better behaviour when eliminating the organic bindings: binder burnout was quicker than that of the first matrix's. Besides, fewer carbonic residues result at the end of the binder burnout phase by using the injection-moulding matrix.

Start-up procedures were optimised through numerous tests. Finally, tests were run in order to determine the voltage–current curve relative to the single cell characterized by the novel matrix (see Figure 4, without support plates curve). Results showed that the cell electric efficiency is 0.29, a low value but the tests are mainly carried out in order to optimise materials and treatment procedures. In fact, a mixture (60% hydrogen, 40% nitrogen) was used as a fuel at the anodic inlet. The cathodic inlet gas was instead composed of CO_2 and air.

The aforesaid tests showed that electrodes surfaces were distorted near the flared holes just after 10 working days; this fact shows that the distribution plates support was not sufficient for electrodes support resulting to be very weak at high temperatures. Thus, original support plates were designed and built in order to avoid cell damage (see Figure 3).

Such plates are constituted by nickel and particular additives: nickel is the main component of the electrodes; additives allow to improve the plates mechanical resistance and the structural stability at high temperatures. Thus, creep and sinterisation problems may be avoided. Numerous channels were created on the plates side which contacts the electrode. The channels allow to correctly distribute the process gases which have to touch the electrodes surface. Holes were made on the support plates surface so that the exhaust and feeding gases could flow. Electrodes were created by tape casting. In fact, tape casting was also chosen as the support plates forma-

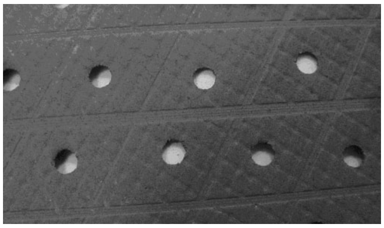

Fig. 3 Picture of the support plates.

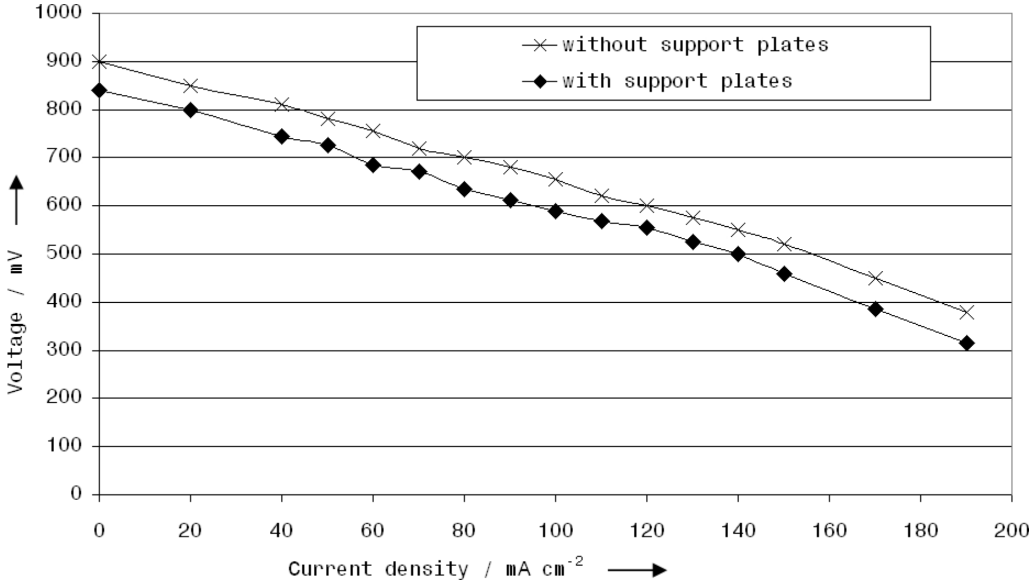

Fig. 4 Cell voltage–current characteristic curve (SCPF tests) (*x*-axis: current–density, mA cm^{-2}; *y*-axis: voltage, mV).

tion technique. The final product is a porous structure which is also used to store carbonates on the anodic side.

The efficacy of the support plates was verified by a measurement campaign. Preliminary tests were carried out in order to determine the optimum quantity of carbonates and the start-up procedure. Voltage–current characteristic was determined (see Figure 4) by using the same fuel flow rate as the previous tests. Cell performances are slightly lower than those obtained without the support plates (cell electric efficiency is 0.26). This fact is due to the following reasons:

- cell electrical resistance increases due to the introduction of the new two elements and their contact resistances;
- feeding gases paths towards electrodes surface are partially hindered by the support plates.

However, higher electrical performances may be obtained by increasing the fuel flow rate. The proposed solution allows to obtain high mechanical resistance: no deformations occurred at the electrodes surface in two working months as verified by microscopy analyses after the experimental tests.

The experimental tests by SCPF showed the versatility and the efficacy of the proposed facility for testing MCFCs materials and solutions. The measurement campaign and microscopy analyses confirmed the validity of the proposed solutions such as the gas distribution system, the stacking system and the heating system characterized by ceramic elements. Tests showed the following improvements when injection-moulding matrices are used rather than those obtained by tape casting:

- the novel matrices are more rigid (cell assembly procedures are quicker and simpler);
- binder burnout phases are quicker and characterized by lower carbonic residues.

Besides, the installation of electrodes support plates allowed to achieve strong improvement of cell mechanical resistance. Cell electrochemical performances are slightly lower than those obtained without the support plates; however, the gas distribution over the electrodes surface may be improved by increasing the cell working pressure. Besides, the electrodes support shape was simplified in the following facility (SCIF). In SCIF, the supports are nettings that reduce the effect of gas hindering between the electrodes and the distribution system.

4 The Single Cell Improved Facility (SCIF)

Tests by SCPF allowed to identify new materials and solutions for cylindrical MCFCs. Thus, a SCIF was built in order to further improve the patented cell performances [1]. Besides, SCIF may already be a prototype close to a commercial fuel cell, differently from SCPF which is only a laboratory facility or a test bench for MCFC materials. A SCIF picture is shown in Figure 5. Its main body is made by a single cell which is constituted by a nickel-chrome porous anode, a lithium aluminate porous matrix (the electrolyte), a nickel-oxide porous cathode and a gas distribution system. The gas distribution system is composed of a series of steel plates, rings and nettings for each electrode compartment (see Figure 6, except for tight ring and netting). A steel separator disk separates the cell from the heating and mechanical external systems. A steel ring in which a steel netting is placed (see distribution ring and netting in Figure 6) contributes to keep the gases' internal flow uniform. This is obtained by choosing a netting diameter smaller than the ring internal one. A steel disk (electrode compartment separation plate) separates the electrode chamber into two sub-chambers. This disk is characterized by holes made in the plate central zone where gases flow from the external sub-chamber, going from the separator disk to the compartment separation plate, to the internal one. A distribution steel netting which is mounted on a ring disk allows to distribute inlet gases on the electrode. Finally, a holed steel ring (the tight ring in Figure 6 without the netting) surrounds the electrode. Exhaust gases flow from the electrode internal sub-chamber to the external environment by the external holes of the disks. They follow paths in the same direction as the inlet gases. Thus, anodic exhaust gases exit at

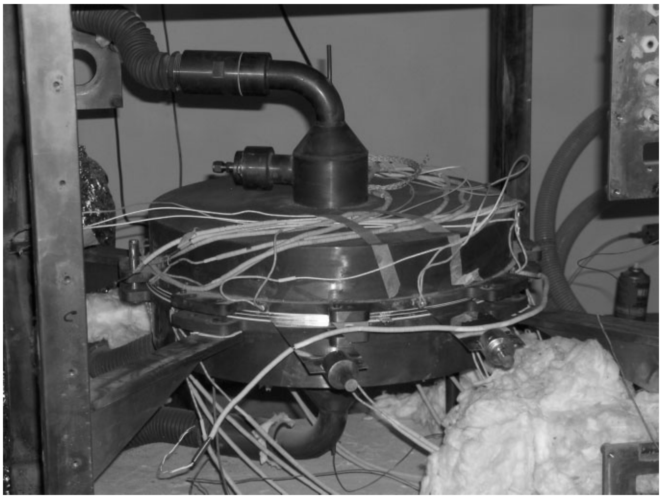

Fig. 5 The SCIF.

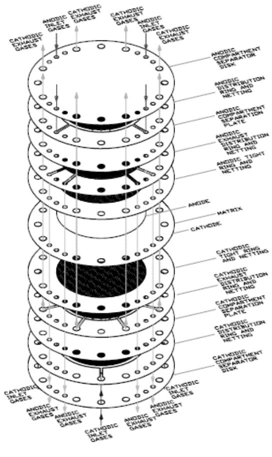

Fig. 6 Assembling distribution system scheme for SCIF and SSMCFC.

the cathodic inlet section, obviously by using different paths (see Figure 6).

Nettings were also introduced to replace the electrodes support elements studied by SCPF. In this way, the cell fabrication process may be simplified and with lower costs. The distribution system is characterized by high mechanical stability for high working temperatures. Steel disks are low rigidity 1 mm thick. Sheets, rings and nettings may be easily formed by water or laser cutting methods with low realisation costs.

The proposed distribution system allows to obtain mechanical, electrical and fluid-dynamical benefits compared to the previous solution (SCPF): a mechanical one because dividing each electrode chamber into two sub-chambers yields a more uniform stack compression strain; an electrical one because the internal electric resistance is reduced by enhancing the contact between two consecutive plates; a fluid-dynamical one because the system based on nettings allows to obtain a more uniform gases distribution inside each chamber. Besides, the proposed distribution system can log catalysts for natural gas reforming which will be a future cell development.

Furthermore, SCIF is completed by a mechanical frame for cell stacking which is equipped with cup-springs to compress the stack, the heating system for cell conditioning (binder burnout, start-up) and gas heating which is constituted by electric resistors, the exhaust and inlet manifolds.

The facility is covered by thermal insulation panels made by ceramic fibres which guarantee external surface temperature lower than 50 °C when cell temperature is 645 °C.

5 Experimental Tests by SCIF

Experimental tests were carried out to determine the SCIF Volt–Ampere characteristic for different working conditions. After binder burnout and start-up procedures, a 0.06 Ohm electric load was applied to the single cell. Hydrogen was used as a fuel in the tests (flow rate at the anodic inlet is about 27 Nl h^{-1}). The cathodic inlet gas was composed of CO_2 and air (respectively about 100 Nl h^{-1} of air, 25 Nl h^{-1} of CO_2). Besides, tests were carried out by supplying steam to the cathodic inlet. For the first 120 working hours, cell voltage diminishing rate is approximately 0.1 V/50 h when no steam is used at the cathodic inlet (see Figure 7); after this period, steam (its flow rate is about 0.02 l h^{-1}) was injected to the cathodic compartment: voltage rose up to a constant value.

Working temperatures were measured by a thermocouple into anodic and cathodic external sub-chambers: temperatures range is 640–645 °C during testing.

Figure 8 shows Volt–Ampere characteristic for the following conditions:

a) when the electric load was applied (0 working hours, no steam at the cathodic inlet);
b) 120 working hours (no steam at the cathodic inlet);
c) 200 working hours (steam at the cathodic inlet);
d) cell temperature was reduced to 400 °C and inlet gases were not supplied to the cell after 200 working hours. After 48 h, cell temperature was increased to 645 °C and gases were supplied again; steam (flow rate about 0.02 l h^{-1}) was injected to the cathodic inlet since a 0.06 Ohm electric load was applied and V–I characteristic was evaluated.

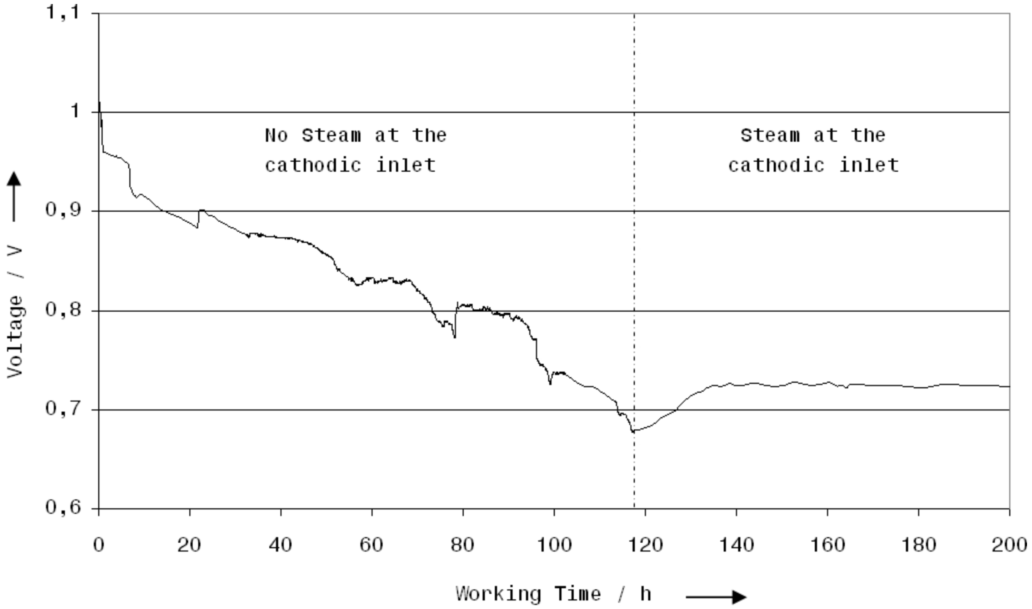

Fig. 7 Cell–voltage *versus* working time (SCIF tests) (*x*-axis: working time, h; *y*-axis: voltage, V).

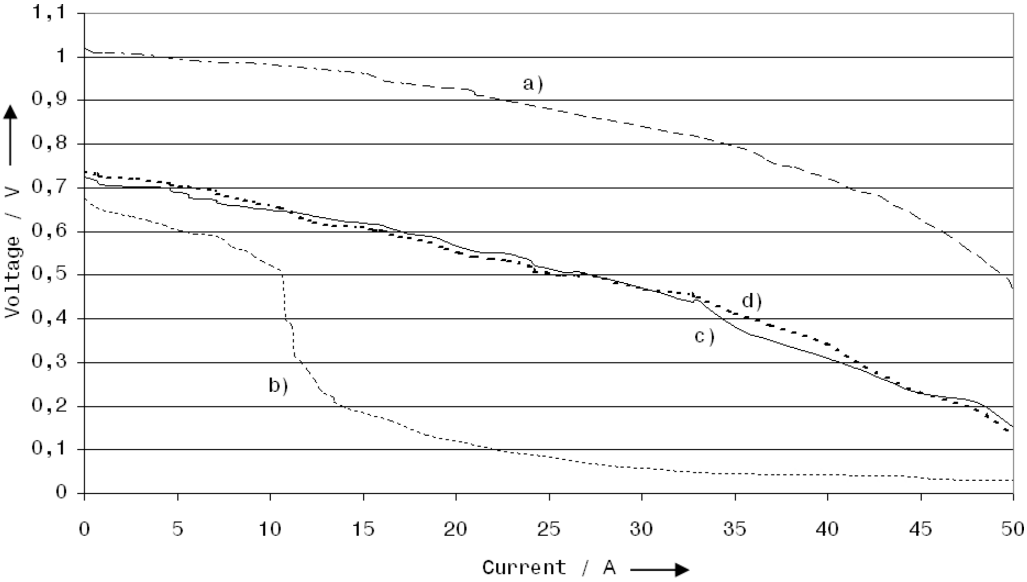

Fig. 8 Cell voltage–current characteristic curves for (a–d) working conditions (SCIF tests) (*x*-axis: current, A; *y*-axis: voltage, V).

Figure 9 shows cell electric power *versus* voltage curves for (a–d) conditions. It is shown that maximum power is respectively about 29.1 W for (a) condition, 5.3 W for (b) condition, 14.6 W for (c) condition and 14.9 W for (d) condition. Single cell area is 250 cm^2. Thus, maximum power densities are respectively:

- 116.5 mW cm^{-2} for (a) condition, which corresponds to a 171.1 mA cm^{-2} current density;
- 21.4 mW cm^{-2} for (b) condition, which corresponds to a 42.7 mA cm^{-2} current density;
- 58.4 mW cm^{-2} for (c) condition, which corresponds to a 132.1 mA cm^{-2} current density;
- 59.6 mW cm^{-2} for (d) condition, which corresponds to a 131.1 mA cm^{-2} current density.

Thus, tests verified that steam supplying at the cathodic inlet is necessary for increasing the cell life and improving its performance.

6 The Cylindrical MCFC Final Configuration

Tests by SCPF and SCIF allowed to determine the optimum configuration for cylindrical patented SSMCFC: a 1 kW stack made by 15 single cells was built and tested. Voltage–

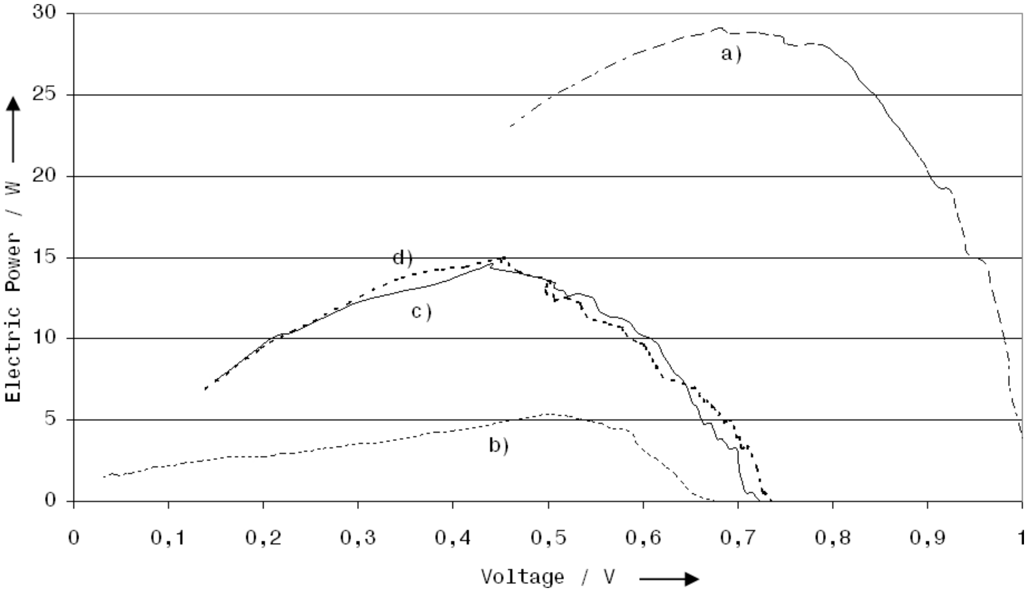

Fig. 9 Cell power density–voltage characteristic curve for (a–d) working conditions (SCIF tests) (*x*-axis: voltage, V; *y*-axis: electric power, W).

current characteristic was identified and maximum power density was measured. A durability test was run.

The SSMCFC configuration is composed of 15 single cells, constituted by a nickel–chrome porous anode, a lithium aluminate porous matrix (the electrolyte) and a nickel-oxide porous cathode. The gas distribution system is made up of low rigidity steel plates and nettings. The assembling sequence is the same as SCIF, but a tight netting is added for each electrode chamber (see Figure 6). It was verified that the proposed new distribution system is characterized by higher mechanical stability for high working temperatures. It allows to attain uniform stack compression strain, uniform gases distribution and the reduction of internal electric resistance by enhancing the contact between the electrodes and the distribution system. Besides, the distribution system can log catalysts for natural gas reforming which are being tested. Sheets and nettings may be easily formed by water or laser cutting methods with low realisation costs in a way similar to SCIF one. A recirculation pipe is also installed starting from the anodic outlet for supplying the produced CO_2 to the cathodic inlet.

The main innovation of SSMCFC is the mechanical frame for cell stacking which was equipped with cup-springs to compress the stack (see Figure 10). The compression system was modified with respect to SCIF in order to improve the uniformity of the compression strain given by the headboards to the stack. Four external ties were added which work in the plate central area. Thus, compression strain is uniformly distributed among the ties in the external stack area and eight ties in the plate external edge. This is obtained by a leaf spring system. In this way, compression strain distribution may be regulated in the conditioning phase, when organic bindings are eliminated.

The SSMCFC heating system for cell conditioning (binder burnout, start-up) and gas heating is constituted by ceramic band resistors applied on the stack external surface. Thus, a uniform heat distribution is achieved also for stacks constituted by a great number of single cells.

SSMCFC is completed by the exhaust and inlet manifolds and the same thermal insulation panels used for SCIF configuration. The final configuration stacking system scheme is reported in Figure 10. Figure 11 shows the proposed 1 kW SSMCFC equipped by a metallic vessel and the control and monitoring system.

In fact, a control and monitoring system for SSMCFC was realized. A graphic interface was also implemented. This system is constituted by the following subsystems:

- thermal subsystem: it is able to monitor stack internal temperatures by thermocouples and a data acquisition module. A PID regulation is also applied to the stack heating system.
- electric subsystem: it monitors single cell voltage, stack current and voltage by Hall effect probes, inconel wires and data acquisition modules.
- flow rate subsystem: it controls and monitors the supplying gas flow rates by mass-flow probes, electrovalves and data acquisition and control modules.

7 Experimental Tests on The SSMCFC Final Configuration

Experimental tests were carried out to identify the 1 kW SSMCFC Volt–Ampere characteristic. Tests were carried out by supplying steam to the cathodic compartment after binder burnout and start-up procedures. Working temperatures were measured by thermocouples into anodic and cathodic external sub-chambers: temperatures range is 645–650 °C during testing.

Fuel used in the tests was hydrogen. The flow rate at the anodic inlet is about 1,100 Nl h^{-1} of hydrogen, at the cathodic

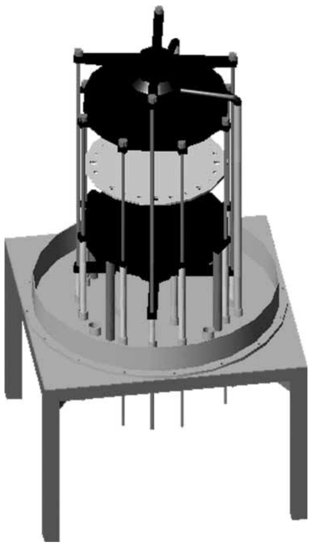

Fig. 10 The final configuration SSMCFC scheme.

Fig. 11 Picture of the 1 kW final configuration SSMCFC.

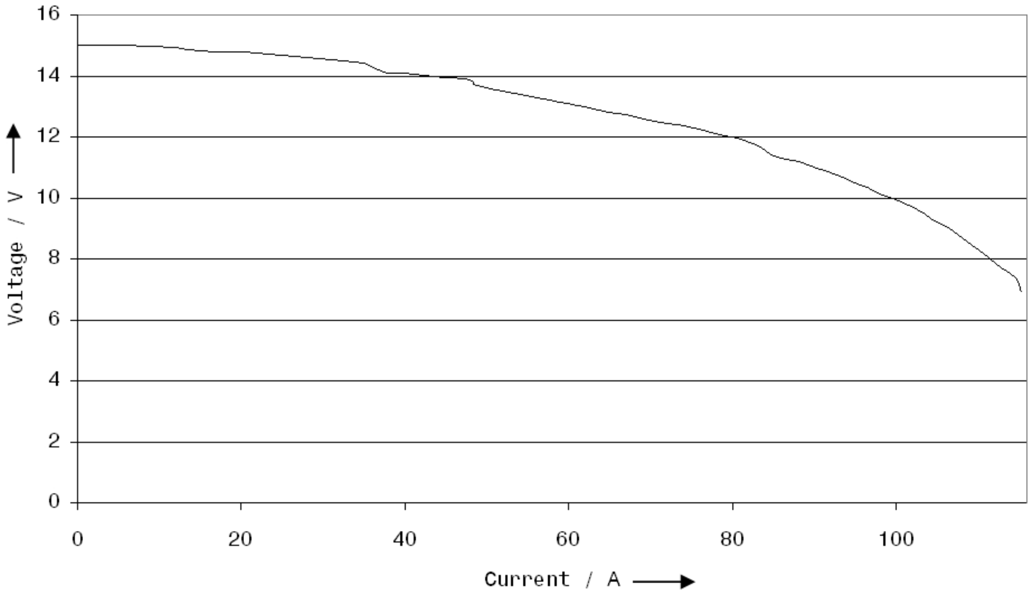

Fig. 12 1 kW SSMCFC voltage–current characteristic curve after about 1,500 working hours (*x*-axis: current, A; *y*-axis: voltage, V).

inlet is about 3,900 Nl h^{-1} of air, 0.8 l h^{-1} of steam. CO_2 at the cathodic inlet is recirculated from the anodic outlet.

Figure 12 shows Volt–Ampere characteristic after about 1,500 working hours. The proposed SSMCFC was able to work with no technical problems for 4,500 working hours (durability test was stopped after 4,500 h). The maximum power attained is about 996 W. A single cell area is 706 cm^2. Thus, maximum power density is 94.0 mW cm^{-2} and maximum current density is 136.9 mA cm^{-2}.

8 Conclusion

Materials, working procedures and improving performance solutions for a cylindrical SSMCFC were investigated in two test facilities. Finally, the optimised configuration of the SSMCFC was tested attaining good results. SSMCFC main peculiarity is the innovative stack design involving cylindrical compact geometry and original gases arrangements. Main SSMCFC technology benefits are high electrical efficiency (up to 40%), thermal self-sustain conditions kept down to kW-size stack because of minimum heat losses due to cylindrical geometry and gas recirculation, non-pressurized devices, long-life (the proposed SSMCFC worked for 4,500 working hours), compact design, modularity thank to internal manifolds, low external temperature. Tests were carried out by hydrogen as a fuel; multi-fuel is actually possible by reforming stages, but the distribution system can log catalysts for natural gas reforming which are actually under test.

Thus, SSMCFC characteristics make the proposed technology suitable for µCHP fuel cell applications because of high performances compared to low realisation costs and viability for industrialisation processes.

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