

Development of planar SOFC device using screen-printing technology.

D. Rotureau*, J-P. Viricelle*, C.Pijolat*, N. Caillol °, M. Pijolat°

Ecole Nationale Supérieure des Mines, LPMG-UMR CNRS 5148

* Département Microsystèmes Instrumentation et Capteurs Chimiques

° Département PROCédés et Evolution des Systèmes avec Solides

Centre SPIN, 158 Cours Fauriel, 42023 Saint-Etienne (France)

Abstract

The aim of this study is to investigate the potentialities of screen-printing technology to manufacture planar SOFC device. Widely studied materials were chosen for this work, particularly YSZ as electrolyte, LSM as cathode and Ni-YSZ cermet for the anode. This technique was firstly used to elaborate the porous electrodes and the collectors constituted by a gold grid. These layers were deposited onto sintered YSZ pellets and two types of fuel cells were produced : conventional two-chamber devices where anode and cathode atmospheres are separate and single chamber fuel cells (SCFC) where the electrodes are deposited on the same electrolyte side and are in contact with a common surrounding atmosphere. Two test benches were developed to study the cells' performances in separate hydrogen / oxygen atmospheres for conventional device or in a unique methane / oxygen mixture for single chamber device. At this point of the study, performances are not optimized and weak power density are available , around 1,2 mW/cm² for SCFC at 800°C with a ratio of methane to oxygen equal to 1,5. Performances of two-chamber devices are also weak due to the electrolyte thickness around 1mm and the low experimental temperature, 500°C. However, the results confirm the feasibility of SCFC and developed test benches constitute a tool for further investigations of modified devices, especially with YSZ electrolyte thick film supported on interconnect materials as no tightness is required for SCFC, or multi-layered electrodes.

Keywords: fuel cell (E), thick films (A), electrical properties (C), YSZ, LSM.

I INTRODUCTION

Over the last twenty years, many chemical gas sensors based on mixed potential phenomena have been developed¹⁻³. These devices consist in a solid electrolyte associated with two electrodes located in the same gas mixture. We have extensively studied a system composed of a β -alumina electrolyte with two metallic electrodes (one in gold, the other in platinum)⁴ and proposed a detection mechanism based on the difference of electrode catalytic activity and their ideally polarizable properties^{2,5}. Such devices are similar to single chamber fuel cells (SCFC) which have been mainly studied by Hibino and co-workers⁶⁻⁷.

The working principle is based on a difference of catalytic activity of the electrodes resulting in preferential reactions with fuel or with air : the anode has a higher activity for fuel oxidation whereas the cathode is more efficient for oxygen reduction^{6,8}. However, the major difference with our β -alumina sensor is the possible exchange of O^{2-} anions of the SCFC electrolyte with the atmosphere, leading to the fuel cell process, contrary to Na^+ cations contained in β -alumina.

The advantages of SCFC compared to conventional SOFC are that there is no need to separate the supply of fuel and air and to decrease the electrolyte thickness as the electrodes are placed on the same surface. The electrolyte ohmic resistance can be decreased by reducing the gap between the two electrodes⁶. Hence, the construction of the SCFC is simplified and low cost planar technology such as screen-printing can be used.

The aim of this study is to investigate the potentialities of screen-printing technology in manufacturing planar SOFC devices. Widely studied materials were chosen to work with, particularly YSZ as electrolyte, LSM as cathode and Ni-YSZ cermet for the anode. As it may be difficult to obtain dense layer for the electrolyte by screen-printing technology, our activity was firstly focused on screen-printing electrodes deposited on sintered YSZ pellets. We

studied the electrical performances of unit cells in a conventional configuration (electrodes on both sides of the electrolyte, with two gas chambers) and the single chamber configuration with 2 electrodes on the same surface : preliminary results obtained are presented in this paper.

II EXPERIMENTAL

Anode, cathode and electrolyte were prepared from commercial powders. YSZ and LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_2\text{O}_3$) were purchased from Superconductive (USA), and a NiO powder from Merck was used with the previous YSZ powder for the anode cermet. YSZ electrolyte used as the support of the fuel cell is prepared by an uniaxial pressing at 50MPa of pellets (diameter 18mm after sintering). The electrolyte is then sintered at 1380°C during 2 hours under ambient air with a temperature rate of 15°C/min for both heating and cooling and the thickness of the final pellets is around 1mm. The inks for electrode deposition by screen-printing are prepared using commercial organic binder (ESL V400-A) and solvent (ESL 400 thinner). The powders, LSM for the cathode and NiO-YSZ with a weight ratio of 50/50 for the anode are mixed with the binder (70% powder / 30% binder) and a few droplets of the solvent are added to reach the desired viscosity. The obtained inks are then deposited directly onto the sintered YSZ pellets, with a semi-automatic AUREL C890 screen-printer machine, using a 180-mesh mask. After deposition, the layers are firstly dried at 100°C for 10 minutes. Then, the electrodes are simultaneously annealed at 1200°C during 2 hours. The thickness of the resulting layers obtained with one deposit is around 20µm. The geometry of the devices depends on the fuel cell configuration. For conventional two-chamber test, electrodes (10mm diameter disc) are deposited on both sides of the electrolyte pellet (Fig. 1). For the SCFC, the electrodes (6×6 mm² square) are placed on the same surface (Fig. 2). The space between electrodes is 1mm. The final preparation step is the deposition of a gold current collector

consisting in a grid (line space of 0.5 mm, Fig. 1 and 2) deposited by screen printing of a commercial glass free ink (ESL 8880H), annealed at 980 during 2 hours.

Before testing performances, fuel cells' constituents are characterised using conventional techniques for structural and textural properties (X-Ray diffraction, specific area measurement, Hg-porosimetry). Electrical measurements are AC impedance spectroscopy with HP 4192A analyser and Van der Pauw DC measurements ⁹.

For conventional two-chamber measurements, a test bench consisting in two concentric tubes and a furnace was developed (Fig. 3). The alumina inner tube is the anode chamber where hydrogen is injected. The unit fuel cell (YSZ pellet) is stuck to the extremity of this tube thanks to a ceramic cement which guaranties the tightness between the two compartments for temperatures under 600°C. This cement constitutes the main limitation of this equipment. The quartz outer tube constitutes the cathode chamber. The contacts with gold collectors are established with Pt wires stuck onto the grid with the same gold paste used for its elaboration. The gas flow and composition in each chamber (O_2/N_2 and H_2/N_2) are set and controlled with mass flowmeters.

The test bench for SCFC is simpler as there is no need to separate the atmosphere surrounding the anode and the cathode. It consist in a single quartz tube placed in a furnace. Electrical contacts are made by mechanicals contacts of gold points and linked to Pt wires. In this case, the fuel is a mixture of oxygen and methane balanced with nitrogen. This test bench allows to perform measurements up to 900°C.

In both single and double chambers' configurations, the cells' performances are determined by the characteristics polarization curves obtained by discharging in a variable resistance.

III RESULTS

III 1 MATERIALS CHARACTERISATION

YSZ commercial powder presents a specific area of 20 m²/g. For electrical measurements, two Pt electrodes were deposited by sputtering on both sides of the pellet. Impedance tests were carried out in the temperature range 500-800°C under air flow (8L/h). The Arrhenius plot of the total conductivity leads to an activation energy of 1,1 eV and the value of conductivity extrapolated to 1000°C is 0,12 S/cm, which is in good agreement with published values for sintered YSZ ¹⁰.

The specific area of the NiO powder used for the anode preparation is 60 m²/g which indicates that this powder is thinner than YSZ one. The weight ratio of 50/50 for NiO/YSZ cermet was chosen following commercial supported anodes specifications. The anodes, due to the presence of NiO, need to be reduced before fuel cell applications. The reduction is performed in situ with hydrogen for the two-chamber device. For SCFC, the reduction is performed during a 3 hours pre-treatment under hydrogen at 650°C. We have checked thanks to thermo gravimetric analysis and X-Ray diffraction that such a treatment leads to a total reduction. The experimental weight loss corresponding to the reduction of NiO into Ni is 10,8 % which is in good agreement with the theoretical value of 10,7%, for equimassic cermet NiO-YSZ. Furthermore no more NiO phases is detected by XRD.

LSM powder has a specific area of 4 m²/g. For LSM screen-printed layers sintered at 1200°C during 2 hours, this value is decreased to 1 m²/g and a residual porosity of 60% is measured by Hg porosimetry. LSM conductivity was obtained by Van Der Pauw's four point measuring method ⁹. The variation of conductivity versus temperature is shown in Fig. 4. At 1000°C the measured value of 120 S/cm is in good agreement with published values ¹⁰.

III 2 FUEL CELL PERFORMANCES

Preliminary tests performed in the two-chamber test bench were carried out at 500°C due to the current limitation of tightness with the ceramic cement as previously mentioned.

Characteristic polarisation curves obtained with H₂ 4 vol.% and O₂ 20 vol.% respectively in anode and cathode compartment are shown in Fig. 5. The open circuit tension is 550 mV and the maximum current density in these conditions is 0,09 mA/cm². A maximum power density of 15 μW/cm² is available.

These low values can be explained by the low temperature used, 500°C, and the large thickness of the electrolyte : considering the conductivity measured at 500°C of 3,2×10⁻⁴ S/cm, the internal resistance of the electrolyte is 310 Ω in these conditions. The interest of this test bench is to study the influence of a single parameter at a time(materials, gas composition...), the others being fixed. For example, the influenced of H₂ concentration in anode compartment at a constant flow rate of 5L/h, at 500°C, with O₂ 20 vol.% in cathode chamber is represented in Fig. 6. The performances are multiplied by 6 when the hydrogen concentration changes from 4 % to 100 %.

In the case of SCFC, tests were performed at 800°C with a mixture of methane (3,5L/h) and air (11,2L/h) corresponding to a volume ratio CH₄/O₂ equal to 1,5. Hibino⁶ obtained highest performances with a fuel to oxygen ratio in the range 1 to 1,5 for the Ni/YSZ/LSM system. Indeed, higher methane proportion can lead to carbon formation.

It is interesting to note that preliminary tests performed with a pure Ni anode instead of a Ni-YSZ cermet did not lead to stable electrical performances as a rapid degradation of the anode was observed. With the Ni-YSZ/YSZ/LSM device and previous conditions, a maximum power of 650 μW/cm² and maximum current density of 4 mA/cm² were measured. However, if the gold collector of the anode is covered with a platinum paste, the performances are improved by a gain of nearly 2 (Fig. 7).

Effectively, the principle of the SCFC is based on a difference of catalytic activity between the two electrodes. Au and Pt mesh collectors respectively for the cathode and the anode, like in Hibino device ⁶, reinforce this difference, resulting in improved performances.

CONCLUSION

During this study, we have developed 2 tests benches allowing to use the conventional two-chamber geometry or a more original single chamber configuration. These equipments constitute a tool for further studies. It is possible to compare the influence of various parameters (material, electrode geometry, multi-layered electrode...) on the cell performances. Screen-printing appears as a practical technology to elaborate at least the electrodes for conventional devices. We have also confirmed the interest of SCFC which can be easily improved. Especially, in this case, no dense electrolyte is required and our current investigations are focused on systems entirely manufactured by screen-printing.

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Figure captions

Figure 1 : Conventional two-chamber fuel cell

Figure 2 : Single chamber fuel cell

Figure 3 : two-chamber test bench

Figure 4 : Conductivity of LSM cathode under air measured with Van Der Pauw method.

Figure 5 : Characteristics of the two-chamber fuel cell tested at 500°C with H₂ 4% O₂ 20%.

Figure 6 : Influence of H₂ concentration on two-chamber fuel performance at 500°C, with 20 vol% O₂ in cathode compartment.

Figure 7 : Characteristic of the SCFC (Ni-YSZ/YSZ/LSM) at 800°C, under air and methane (CH₄/O₂ = 1,5). The anode gold collector is covered with platinum.

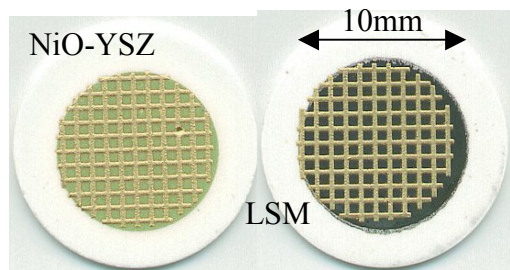


Figure 1

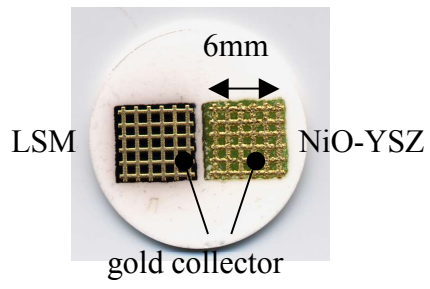


figure 2

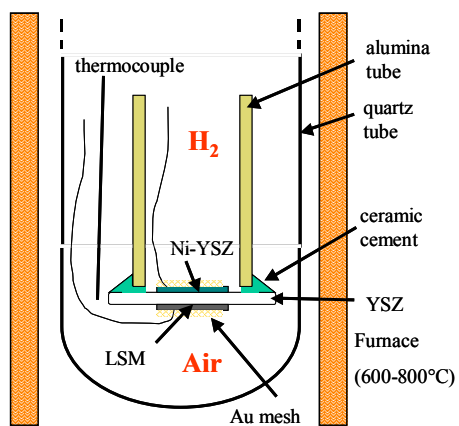


figure 3

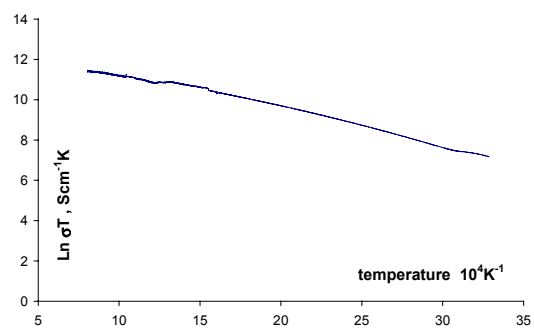


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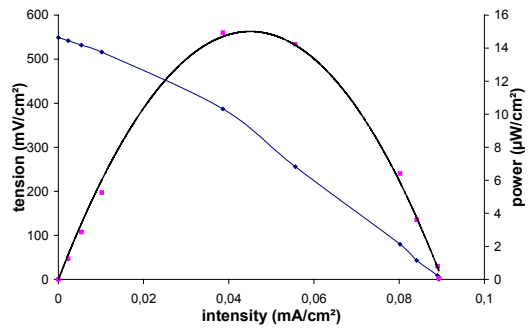


figure 5

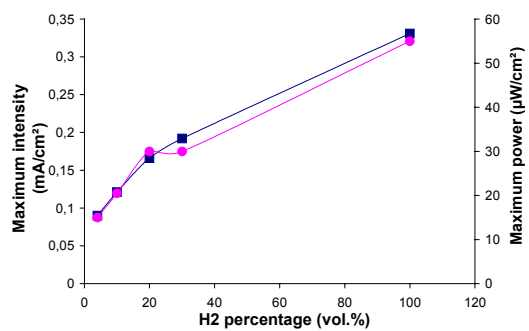


figure 6

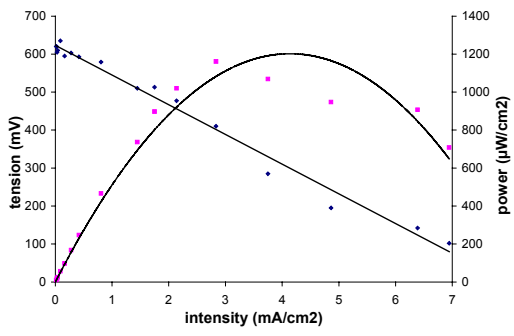


figure 7