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Compatibility of screen-printing technology with micro-hotplate for gas sensor and solid oxide micro fuel cell development

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Abstract

Screen-printing technology is widely used in the field of gas sensors and can also be used to fabricate electrodes for solid oxide fuel cell (SOFC). The compatibility of this technique with micro-hotplate is studied to produce micro sensors and micro SOFC. For sensors application, development of inks containing precursor of sensing element allows to decrease annealing temperature and to improve adhesion. For SOFC development, we investigated a new type of device named single-chamber fuel cell (SCFC) for which the fuel and the oxygen are mixed and in contact with both the anode and cathode. Such devices were firstly built at a millimeter scale using LSM for cathode, YSZ for electrolyte and Ni-YSZ cermet for anode. Two types of configuration were studied: SCFC developed on YSZ support with screen-printed electrodes, and SCFC entirely manufactured by screen-printing on a inert ceramic substrate made of alumina. Although weak power densities were measured, around 1 mW/cm^2, the feasibility of SCFC was confirmed. Then, preliminary results concerning LSM cathode deposition on micro-hotplate were obtained. LSM layers annealed up to 800 °C resist well to temperature cycling but exhibit low conductivity.

Keywords: Screen-printing; Gas sensors; Solid oxide fuel cell; Single chamber; Micro-hotplate

1. Introduction

It can be expected that research and commercial interests in hydrogen technology and fuel cells will continue to grow during the next coming years. Several research directions are driven by microtechnology. One direction includes the development of sensor systems for monitoring the fuel gas concentrations and the operation of fuel cells. Another research topic is the microtechnological implementation of micro fuel cell modules as power supply. The future vision would be to create, e.g. autarkic sensor systems, where the power supply, the sensors for micro fuel cell operation and the application-specific sensors are integrated in a single device.

The fabrication of sensors and solid oxide fuel cell (SOFC) modules in microtechnology is particularly challenging since high operating temperatures of several hundred degrees are needed [1]. In this study, the compatibility between screen-printing technology and micro machined substrates is investigated. Screen-printing is widely used in the sensor field to deposit sensing films with a few micrometers' thickness, and also suits well to deposit porous electrodes for SOFC. This technique is easily transferable to mass production but it is usually applied with conventional ceramic substrates and not with micro-hotplates. In this case, three major problems have to be solved: the positioning of the deposits, the mechanical resistance of the micro-hotplate and the adhesion and functional properties of the resulting layer (Fig. 1). The two first technological difficulties may be clear up thanks to adjustment of depositions parameters. For the two latter, the composition of the screen-printed inks has to be optimized.

The first example presented in this paper concerns the development of tin dioxide sensor on micro-hotplate. Particular SnO_2 inks are developed to improve layer adhesion while keeping satisfying electrical properties. The second example deals with particular SOFC, single-chamber fuel cell (SCFC) for which no separation of fuel and oxygen by the electrolyte is required. The two gases are mixed and are in contact with both electrodes [2,3]. The principle of such device is based on the selective catalytic activity of each electrode towards the considered gas: fuel oxidation at the anode and oxygen reduction at the cathode. The main advantage of SCFC is that no gas separation is required. Hence, the design and the technology for their development is

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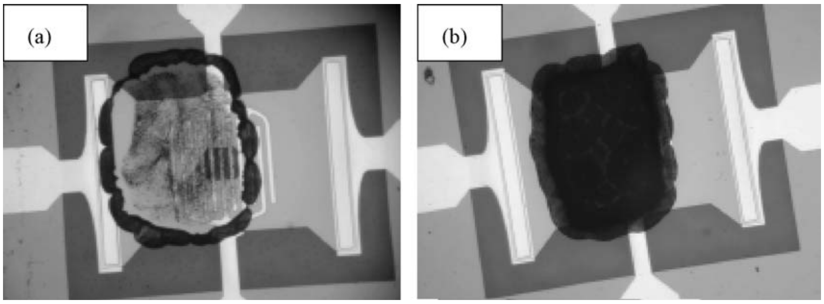

Fig. 1. SnO_2 thick film (350 μm × 500 μm) deposited by screen-printing on a micro-hotplate for gas sensor application; (a) problems of positioning and adhesion and (b) functional SnO_2 layer.

quite simplified compared to conventional SOFC, especially in regards of miniaturization. We firstly investigated the feasibility of a SCFC at a millimeter scale, using well-known materials for SOFC: LSM ($La_{0.8}Sr_{0.2}MnO_3$) for cathode, YSZ (Yittria (8 mol%) Stabilized Zirconia) for electrolyte and Ni-YSZ cermet for anode. These materials are not optimized for SCFC concept, but the objectives of this study are to show the feasibility and to demonstrate possibilities of miniaturization rather than to obtain high performances. The first studied SCFC device is supported on sintered YSZ electrolyte. Then, in order to miniaturize this system, a SCFC entirely manufactured by screen-printing on alumina substrate was studied. Finally, in order to go to further miniaturization, preliminary tests of deposition of LSM cathode by screen-printing on micro-hotplate were conducted.

2. Results

2.1. SnO_2 sensor development on micro-hotplate

For tin oxide gas sensor development, a conventional ink would be constituted of the active material (SnO_2) and of volatile and permanent binders in order to control, respectively, the rheological properties for the deposit and the adhesion of the resulting material onto the substrate [4]. As permanent binders are usually glasses that are electrical insulators, some problems of SnO_2 percolation strongly decrease the conductivity. Hence, a new ink without mineral binder has been developed. However, in this case, some problems of layer adhesion are encountered (Fig. 1a). To solve this point, a Sn alkoxide precursor has been introduced in the ink, leading to the formation of SnO_2 during thermal annealing. Various ink compositions have been studied (Table 1). The conductance's under air and under 300 ppm CO at 500 °C of the corresponding sensors obtained after annealing of the layers at 650 °C are shown in Fig. 2. Inks A and B containing no organic binder leads to cracked layers, explaining the low sensor conductance. Layers resulting from inks C to F were quite homogeneous and presented a good adhesion (Fig. 1b). The lower conductance of sensors issued from inks C and D is explained by the higher porosity of these layers due to the higher alkoxide content.

Table 1
Composition (wt%) of SnO_2 inks

Inks	SnO_2	Alkoxide	Organic binder
A	63	37	0
B	50	50	0
C	67	26	7
D	64	26	10
E	66	17	17
F	61	15	24

Thus, by adjusting the screen-printing parameters and the ink composition, it has been possible to improve the alignment on the micro-hotplate and to reduce the annealing temperature to 650 °C, while keeping a good adhesion and electrical performances.

2.2. SCFC development

The new concept of single chamber [2,3], allows development of planar devices running in a mixture of fuel and air. In this case, screen-printing technology is well adapted to deposit the two porous electrodes but also the electrolyte as a high densification rate is not required for single chamber SOFC.

2.2.1. YSZ-supported SCFC

In order to confirm SCFC concept and to set up a measurement bench for SOFC, the first devices were built at a millimeter scale on YSZ pellets for the electrolyte. Then, the two electrodes, LSM and Ni-YSZ cermet were deposited by screen-printing on the YSZ pellet. The inks were constituted of the initial powders, either LSM or a mixture of NiO and YSZ (50–50 wt%) with organic binder and solvent. The layers were annealed at 1200 °C during 2 h [5]. Then, two gold collectors were also deposited by screen-printing in the form of a grid (Fig. 3). The microstruc-

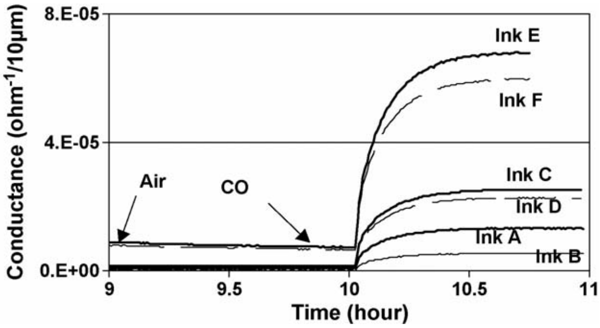

Fig. 2. Influence of SnO_2 ink composition on the conductance (normalized to 10 μm thickness) at 500 °C of sensors obtained after annealing at 650 °C.

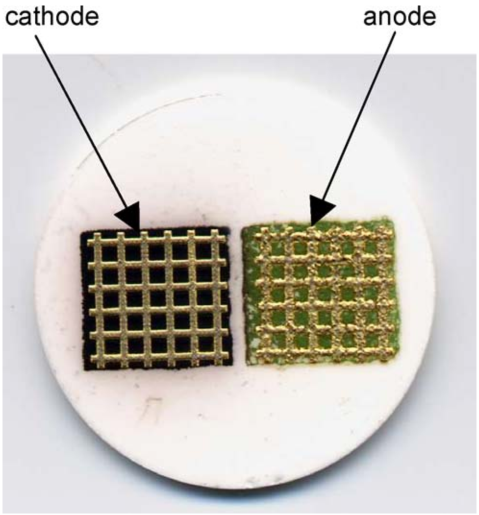

Fig. 3. Single-chamber fuel cell on sintered YSZ pellet, with screen-printed electrodes (6 mm × 6 mm) and collectors.

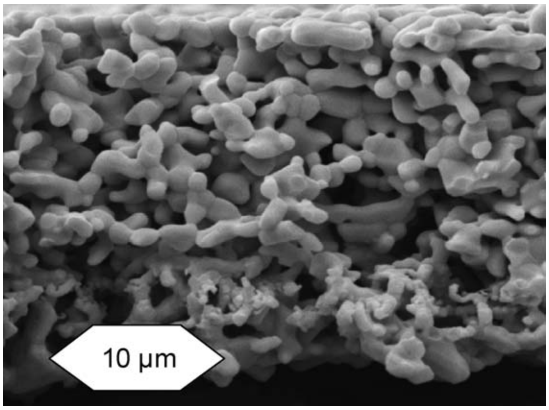

Fig. 4. Cross-section SEM of the LSM porous cathode deposited by screen-printing, annealed at 1200 °C during 2 h.

ture of the materials is shown in Fig. 4 (LSM) and in Fig. 5 (Ni-YSZ/YSZ interface). LSM layers are quite porous, around 60% and homogeneous. The porosity of the cermet anode is similar but their microstructure is quite heterogeneous.

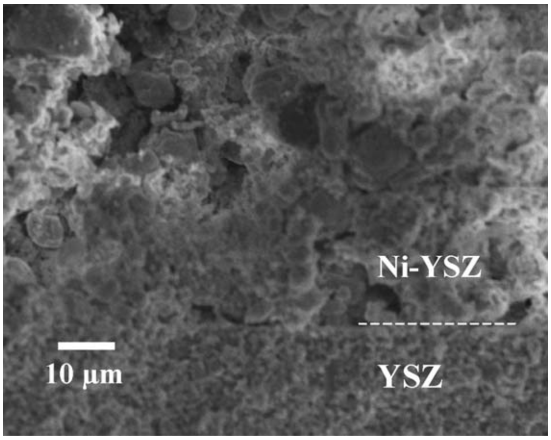

Fig. 5. Cross-section SEM of the Ni-YSZ anode, annealed at 1200 °C during 2 h, deposited by screen-printing on YSZ pellet.

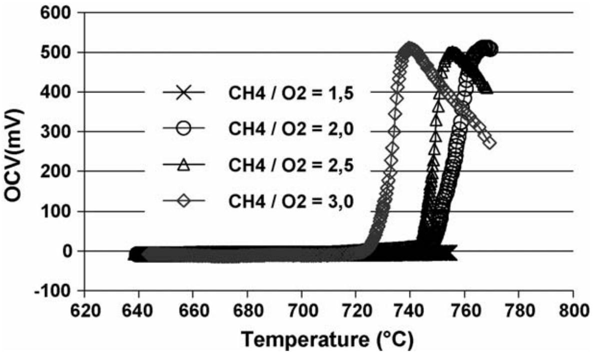

Fig. 6. YSZ-supported SCFC open circuit voltage as a function of temperature and CH_4/O_4 ratio.

The SCFC devices were tested in CH_4/oxygen mixtures with ratio in the range 1.5–3 at various temperatures in a furnace. With our experimental conditions, it can be seen in Fig. 6 that, for a fixed CH_4/oxygen ratio, the temperature range to obtain a significant open circuit voltage (OCV) is quite narrow and strongly depends on the gas ratio. This behavior is explained by the strong influence of the electrode catalytic activity towards CH_4 and oxygen depending on the temperature. At 770 °C, with a ratio CH_4/oxygen equal to 2, a maximum power density of around 1 mW/cm^2 was measured (Fig. 7). This low performance is explained by the non-adequate microstructure of the anode, and not by the SCFC geometry. Effectively, a conventional device elaborated with the same materials, with electrodes on the opposite faces of the YSZ pellet exhibit a maximum power density similar to the SCFC one [5]. This result thus validates the SCFC concept.

2.2.2. *Al_2O_3-supported SCFC*

The second step of the SCFC development with a final objective of miniaturization consists in the development of a device entirely manufactured by screen-printing technology on a self-heated α-Al_2O_3 substrate. Such substrates are commonly used for gas sensor application. In this study, the α-Al_2O_3 rectangular plate (5 mm × 38 mm) is equipped with a platinum resistance of 10 Ω and gold connectors for electrical contacts (Fig. 8a). On the opposite side, a YSZ electrolyte layer (4 mm × 4 mm) is deposited by screen-printing (Fig. 8b). The ink is prepared with the same YSZ powder as for the YSZ pellet previously used. 30 wt% of organic solvent is added to the powder, and two deposits are performed resulting in a final layer of 40 µm after

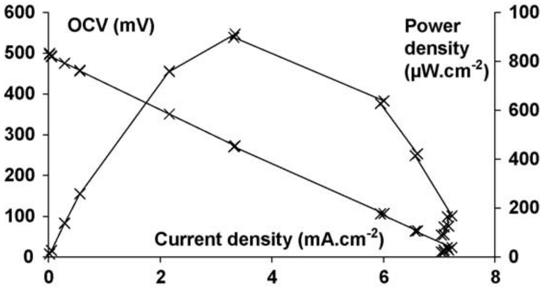

Fig. 7. Polarization curves of the SCFC at 770 °C, with a CH_4/O_4 ratio equal to 2.

Fig. 8. Single-chamber fuel cell supported on alumina substrate: (a) platinum heater and (b) SCFC with screen-printed YSZ (4 mm × 4 mm), NiO-YSZ and LSM electrodes (4 mm × 1 mm) and gold and platinum collectors.

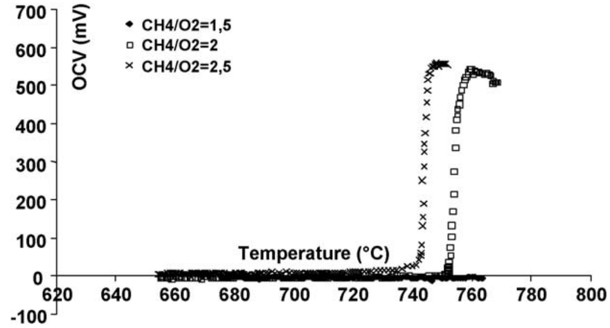

Fig. 10. Alumina-supported SCFC open circuit voltage as a function of temperature and CH_4/O_4 ratio.

annealing at 1380 °C during 2 h. A cross-section micrograph of the YSZ layer is shown in Fig. 9. Despite a high porosity close to 45% as measured by mercury penetration method, its electrical conductivity is satisfying, around 0.1 S/cm at 1000 °C, as it is similar to the one of the YSZ sintered pellet. Then, the LSM cathode and the NiO-YSZ anode (4 mm × 1 mm) are deposited using the same inks as for previous SCFC device on YSZ support, with the same thermal treatment, 1200 °C during 2 h. Finally, metallic collectors, respectively, of gold on the cathode and of platinum on the anode, are also deposited by screen-printing (Fig. 8). The different nature of the metallic collectors reinforces the difference of catalytic activity between the anode and the cathode, which is the basis of the SCFC concept, and allows to improve SCFC performances [2,5].

This new device was firstly tested in a furnace in similar conditions as previous ones for the device on YSZ pellet. In this case, a similar behavior is observed. The open circuit voltage is strongly dependant on the combination of temperature and gas composition. A maximum OCV of nearly 600 mV is obtained at 760 °C with a CH_4/O_2 ratio of 2, or at 750 °C if this ratio is equal to 2.5 (Fig. 10). The maximum power density with such device is also around 1 mW/cm^2. However, if this SCFC prototype is tested in a glass reactor using its own platinum heater instead of a furnace, no significant performances can be measured. This result confirms that the catalytic activity and thus the gas composition and the temperature are crucial parameters which have to be optimized, as well as the choice of electrode materials for the SCFC concept.

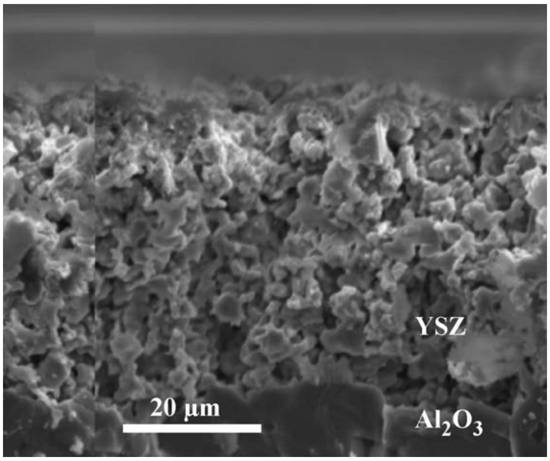

Fig. 9. Cross-section SEM of the YSZ layer deposited by screen-printing on alumina support, annealed at 1380 °C during 2 h.

2.2.3. LSM deposited on micro-hotplates

The third step of this study concerning SCFC development is the miniaturization on micro-hotplate. The three materials (cathode, electrolyte and anode) could be successively deposited by screen-printing. Preliminary results dealing with the LSM cathode deposit are presented here. The micro-hotplates were prepared on silicon wafers by IMT (Neuchâtel) [6]. They consist in a dielectric membrane in which a platinum heater is embedded, and covered on top by electrodes. The heater is made of platinum with a tantalum adhesion layer (225 nm). The platinum film is patterned using a lift-off process. Two low-stress LPCVD silicon nitride films form the thermally insulated 1.0 µm thick membrane of the micro-hotplate. One hundred and fifty nanometer thick platinum/tantalum electrodes are patterned on top of the membrane using a lift-off process. The membrane is released using backside bulk micro-machining of the silicon wafer. The membrane has an area of 1.0 mm × 1.0 mm, and the areas covered by the double meander heater and the electrodes are of 450 µm × 450 µm and of 400 µm × 400 µm, respectively. Four electrodes having 180 µm wide square contacts and a gap of 40 µm between them were patterned as shown in Fig. 11. The power consumption of these micro-hotplates is around 120 mW at 600 °C. They can survive to annealing at 600 °C in an oven, and local temperatures up to 800 °C on hotplate can be reached. LSM films of 450 µm × 450 µm were deposited by screen-printing using the same LSM ink as for previous SCFC devices, on square chips including 7 × 7 membranes. Fig. 12 showing the resulting deposits indicates that 6 membranes over 49 were broken during screen-printing process. For the others, the alignment of the layers on the membranes is correct.

Two types of annealing were performed after LSM screen-printing deposition and drying at 100 °C: (i) annealing of the whole wafer in a furnace at 400 °C during 10 h or at 600 °C during 2 h or (ii) on-chip annealing at 700 or 800 °C during 30 min. Then, on-chip conductivity measurements were performed with a two point mode as the LSM layer resistance is quite high, during a temperature cycle up to 630 °C, using the embed-

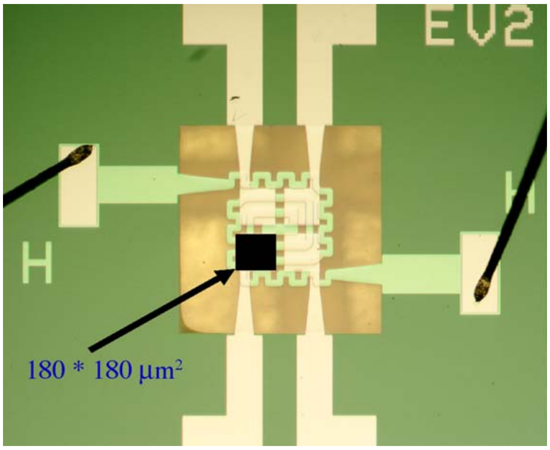

Fig. 11. Photograph of the micro-hotplate with four square electrodes contacts [6].

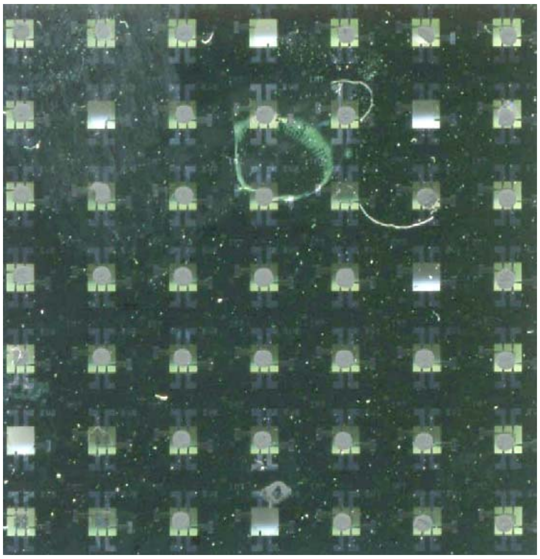

Fig. 12. Photographs of LSM films deposited by screen-printing on chip of 7 × 7 membranes.

ded platinum heater. Variations of resistance versus temperature shown in Fig. 13 indicate that the layers are sufficiently robust to resist to the temperature cycle. However, for 400 °C annealed layers, the resistance evolves and is lower during cycling down.

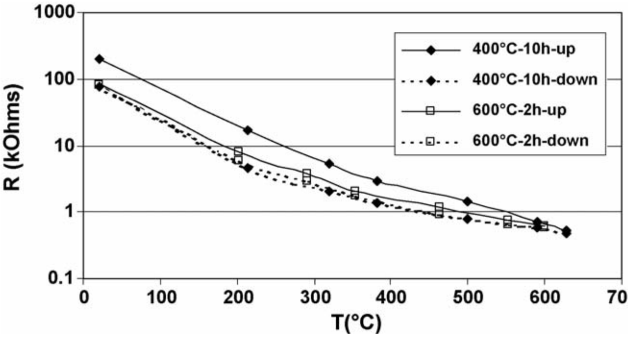

Fig. 13. Resistance variation vs. temperature cycling of two screen-printed LSM films on micro-hotplate: influence of annealing temperature 400 °C, 10 h or 600 °C, 2 h.

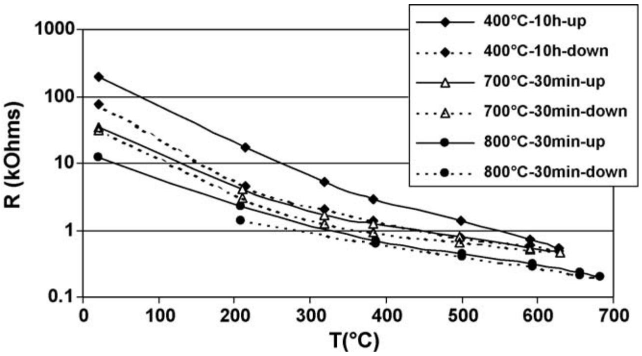

Fig. 14. Resistance variation vs. temperature cycling of screen-printed LSM films on micro-hotplate: influence of high on-chip annealing temperature 700 °C or 800 °C, 30 min compared to 400 °C, 10 h.

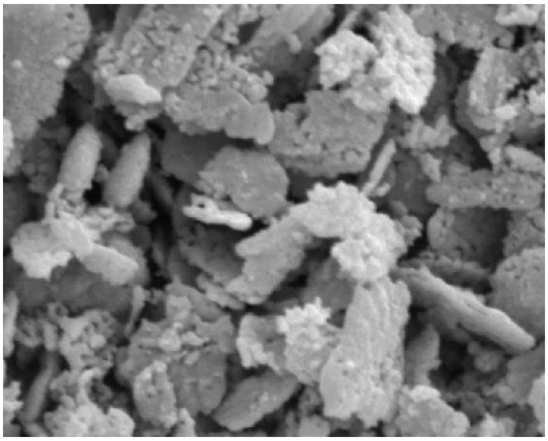

Fig. 15. Cross-section SEM of the LSM cathode deposited by screen-printing, annealed at 1000 °C during 2 h.

On the contrary, for 600 °C treated layers, the resistance is stable and similar for cycle up and down. Moreover, the values are similar for both layers during cycle down. This result proved that on-chip annealing is possible, at least up to 630 °C, and that's why we performed annealing at 700 and 800 °C. However, these higher temperatures don't significantly improve the conductivity of the LSM layer (Fig. 14). The value of conductivity calculated from previous experiments is quite low, around 1 S/cm at 630 °C, with activation energy of 18 kJ/mol. For a sintered material elaborated from the same LSM powder used for ink preparation, the conductivity is around 100 S/cm at 630 °C and the activation energy equal to 9 kJ/mol, which is agreement with values found in the literature This weak conductivity of the LSM layer is explained by the low annealing temperature which not allows the LSM layer sintering as proved by the microscopic observations of layers annealed at 1000 °C (Fig. 15). It is necessary to reach 1200 °C (Fig. 4). to have a sufficient sintering and thus conductivity of the LSM layer.

3. Conclusions

Preliminary results demonstrate that screen-printing is a simple technology which can be compatible with micro-hotplates if the inks are optimized, for various applications. For SnO_2 gas sensors, the problem of layer adhesion due to low acceptable annealing temperature to avoid hotplate damages was solved thanks to a new ink formulation.

For SOFC application, despite weak performances due to non-adequate anode microstructure and non-optimized materials, the SCFC concept was validated. Devices with a simple planar geometry and coplanar electrodes were built and exhibited a power density of around 1 mW/cm^2 in the range 600–700 °C, with an methane–oxygen mixture. Preliminary results for LSM deposits on micro-hotplates, with the objective of SCFC miniaturization, show problems of temperature limitation for the annealing. As for the development of SnO_2 sensors on micro-hotplate, the elaboration of ink including precursors of the desired material (LSM) may be a solution which is under focus.

This paper only presents the feasibility study of material deposition by screen-printing on micro-hotplates. Obviously, many points have to be investigated in more details, such as thermo-mechanical compatibility of chosen materials. Due to past experience with SnO_2 gas sensors, it is known that thickness layers have to be minimized to reduce stress, and, at the moment, temperature are limited to 600 °C due to thermal resistance of micro-hotplates. These problems are still under focus.

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Biographies

J.-P. Viricelle received his Ph.D. in chemical engineering in 1994 at Ecole des Mines of St.Etienne (France). He has worked as a post-doctoral student on the oxidation of ceramic composite materials in University of Limoges (France) from 1995 to 1997. Since 1998, he has been working as a research engineer in MICC department (Microsystems, Instrumentation and Chemical Sensors) attached to SPIN research center (Natural and Industrial Process Sciences) in Ecole des Mines of St.Etienne. His research activity is focused on electrical properties of solids for development of chemical gas sensors, solid oxide fuel cells and micro-reactors.

C. Pijolat is professor of chemical engineering and microsystems at Ecole des Mines of Saint-Etienne (France), he manages the MICC department (Microsystems, Instrumentation and Chemical Sensors) attached to SPIN research center (Natural and Industrial Process Sciences). Since 1980, he has been working in the field of electrical properties of solids and on the development potentiometric and semiconductor sensors. He has contributed to several technological transfers of sensors into industrial applications.

B. Riviere worked as a Ph.D. student in the “Microsystems, Instrumentation and Chemical Sensors” research team from 2000 to 2004. The objective of her research activity was to develop screen-printing technology for gas sensor development and particularly to study the compatibility of this technology with micro-hotplates.

D. Rotureau worked as a Ph.D. student in the “Microsystems, Instrumentation and Chemical Sensors” research team from 2001 to 2005. The objective of his research activity was to develop solid oxide fuel cells on the basis of screen-printing technology and in particular single chamber device requiring no separation between fuel and air.

D. Briand received his B.Eng. degree and M.A.Sc. degree in engineering physics from École Polytechnique in Montréal, in collaboration with the Laboratoire des Matériaux et du Génie Physique (INPG) in Grenoble, France, in 1995 and 1997, respectively. He obtained his Ph.D. degree in the field of micro-chemical systems from the Institute of Microtechnology, University of Neuchâtel, Switzerland, in 2001, where he is currently a project leader. He is in charge of European and industrial projects and of the supervision of doctoral students. His research interests in the field of microsystems include PowerMEMS, polymeric MEMS, the integration of nanostructures on microsystems, and the development of micro-analytical instruments for gas-sensing applications.

N.F. de Rooij received a Ph.D. degree from Twente University of Technology, The Netherlands, in 1978. From 1978 to 1982, he worked at the Research and Development Department of Cordis Europa N.V., The Netherlands. In 1982, he joined the Institute of Microtechnology of the University of Neuchâtel, Switzerland (IMT UNI-NE), as professor and head of the Sensors, Actuators and Microsystems Laboratory. Since October 1990 till October 1996, he was acting as director of the IMT UNI-NE. Since 1987, he has been a lecturer at the Swiss Federal Institute of Technology, Zurich (ETHZ), and since 1989, he has also been a professor at the Swiss Federal Institute of Technology, Lausanne (EPFL). His research activities include microfabricated sensors, actuators and microsystems.