STUDY AND DEVELOPMENT OF MICRO FUEL CELLS

A. Martinent-Beaumont[1], V. Faucheux[1], N. Martin[1], N. Karst[2], JY. Laurent[1]
[1] Department of Nanomaterials, CEA/LITEN, Grenoble, France
[2] STMicroelectronics, Tours, France

Abstract: This work describes our contribution to the development of micro fuel cells running with passive air-breathing conditions (natural convection).

Firstly, the micro fuel cell design is explained: the fuel cell is a succession of thin layers deposited on a silicon substrate and its core lies on PEMFC technology (hydrogen as the fuel). This approach presents the advantage of being easy to miniaturize and easy to integrate in the microelectronics industry.

Next, study of the performances of the micro fuel cell versus external parameters is depicted. Considered parameters are temperature, relative humidity of the air, dry or humidified hydrogen. As expected, all these factors play a major role in the micro fuel cell performances, especially in the hydration of the membrane and the water management of the fuel cell core.

Lastly, when nine of them are connected in series, these emerging systems make it possible to reach more than 2W.

Keywords: micro fuel cell, silicon substrate, PEMFC

1. INTRODUCTION

Currently, power needs of portable devices are drastically increasing. Indeed, the current basic cellular phones need about 800 mW while the most recent sophisticated phones need more than 3 W. Commercialized lithium-ions batteries, which supply most of the cellular phone, are quite limited in term of autonomy (about 200 Wh kg^{-1} and 400 Wh l^{-1}) and their progress potential should be less important than the fuel cells in the years to come.

The development of the miniature fuel cells is mainly performed by two technologies: DMFC (methanol as the fuel) and PEMFC (hydrogen). There are also two strategies concerning the fuel cell's architecture: some tend to miniaturize the traditional fuel cells with stack design while others decide to innovate by using the tools of the microelectronics to conceive micro-fuel cells on silicon wafers for example. These MEMS fuel cells make it possible to consider different substrates and different geometrical factors, which should both reduce the costs (use of 'low cost' substrates like ceramics) and increase the specific surface of the electrodes while reducing their apparent surface. The use of nano materials in the design of the electrodes should also make it possible to increase their active surface.

CEA started micro fuel cell development about 8 years ago. STMicroelectronics, one of the leading semiconductor manufacturers, and CEA signed an agreement to collaborate on the development of new miniaturized energy source solutions 4 years ago. The joint work includes the development from the components to the system, i.e. from the fuel cell core to the assembly, packaging and power management of several interconnected fuel cells.

2. DESCRIPTION OF THE CEA/ST MICRO FUEL CELL TECHNOLOGY

The micro fuel cell design is based on semiconductor technology and its core lies on PEMFC technology (Hydrogen as the fuel). The fuel cell is a succession of thin layers deposited on a silicon wafer. This approach presents the advantage of being easy to miniaturize, contrary to classical fuel cell with stack design, and easy to integrate in the semi-conductor industry.

Fuel is supplied by the way of an innovative safe system which is able to produce hydrogen as a result of chemical hydride hydrolysis.

The core part of the cell consists basically of two electrodes (anode and cathode) separated by a cation-exchange membrane (the electrolyte). Hydrogen diffuses through the gas diffusion layer and is oxidized on anodic catalytic sites at the negative electrode (figure 4) and protons (H^+) are formed on one hand, which run through the membrane, and electrons on the other hand, which generate a current running outside the cell. Electrons react at the positive electrode (the cathode) with protons (H^+) coming from the negative electrode and oxygen from the air. With electricity, the by-products of the reaction are water and heat.

2.1 Detailed process of fabrication

The proton exchange membrane micro fuel cell core (figure 1 and figure 2) is made up of the superposition of several thin layers. Miniaturization is accomplished by employing thin-film deposition techniques (vapor deposition, standard lithographic patterning and several etching processes).

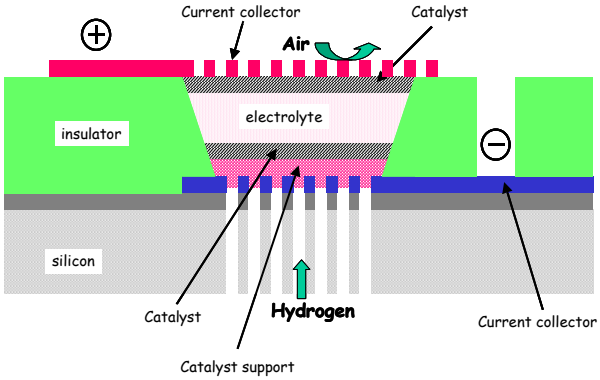

Figure 1. Schematical view of the CEA/ST microPEMFC.

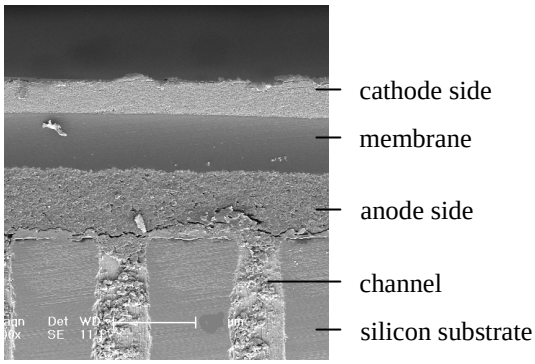

Figure 2. SEM picture of a micro fuel cell.

The first step of the fabrication consists in creating channels by reactive ion etching in the silicon wafer in order to provide the fuel to the catalysts. The anodic gold current collector is then deposited on the substrate by plasma vapor deposition. The third step corresponds to the enduction of a photo-resist resin on the whole wafer. Next the location of each fuel cell core on the wafer is made by insulation of the resin using a mechanical mask. Then the anodic diffusion layer is deposited on each micro fuel cell. It consists of a composite layer of graphite and polymer, which allows to manage water and hydrogen flows. A composite platinum-based ink is then sprayed on the diffusion layer.

A Nafion® solution is deposited on the wafer by serigraphy and dried to form a thin homogeneous solid layer, followed by a heat treatment to reinforce mechanical properties of this layer. The cathode is then put on this membrane by spray of a slurry made of platinated carbon and Nafion® aqueous solution. The cathodic gold current collector is then deposited by PVD as the final layer. Its thickness is enough to ensure a good electronic conductivity and allows to the oxygen of the air to reach the platinum catalyst.

The full layers are less than 100 µm thick. Figure 3 shows a picture of a silicon 8” wafer at the end of the process described above.

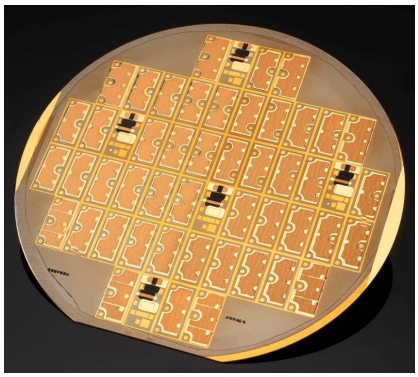

Figure 3. Fuel cells on a 200 mm wafer : each golden dot is a single fuel cell core

3. RESULTS

Performances of each fuel cell are evaluated with hydrogen as fuel and oxygen from the air as the oxidant. Electrochemical measurements are performed on a exclusive tailor-made tool which makes it possible to test every fuel cell of the 8” wafer in a automated environment (Figure 4).

Figure 4. Micro fuel cell test system.

The dual challenge of micro fuel cells is to run them in full passive air-breathing configuration and at the same time to conceive a system as small as possible. A smart architecture of micro fuel cell is being developed in order to avoid using auxiliary systems like pumps, fans and so on. It leads to study and development of

adequate materials of the fuel cell core including the substrate, adequate materials of the packaging (thermal optimization), and an innovative packaging.

Influence of external parameters is then an essential study and the key point is to manage a large range of temperatures and humidity by the use of a smart design.

Figure 5 shows polarization curves of a micro fuel cell running at 30°C with passive air from 10 to 90 % of relative humidity (r.h.). As expected, humidity of both fuel and oxidant plays a major role in the micro fuel cell performances. In the case of 10 % r.h. the fuel cell core is very dry. As a consequence, the Nafion® membrane doesn't succeed to hydrate enough to reach a large range of current. From 50 to 90 % r.h. with a dry H_2, the performances of the micro fuel cell are high, especially in the targeted range of voltage (ie from 1 to 0.5V). In the case of humidified H_2, performances are elevated as soon as 30% r.h. is reached.

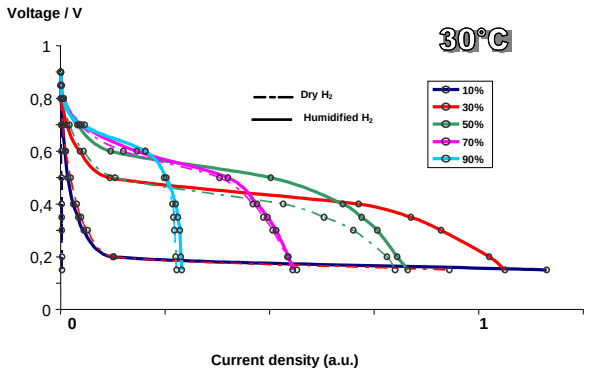

Figure 5. Polarization curves of a microfuel cell running with passive air-breathing system in different relative humidities. Dry Hydrogen: dotted line, humidified Hydrogen : solid line, T°=30°C.

Figure 6 shows polarization curves of a micro fuel cell running at 45°C with passive air from 10 to 70 % of relative humidity (r.h.). As expected, temperature of ambient air plays a major role in the micro fuel cell performances as well, especially in the hydration of the electrolyte and the water management. Indeed, when the fuel cell is running at high temperatures (45°C), the fuel cell never reaches flooding zone. Moreover, performances in high voltage range are much lower than the ones in the case of running at 30°C. It is directly linked to an evaporation phenomenon which is higher at 45°C than at 30°C. Impedance spectra plotted in different static points allowed to estimate internal resistance: the smallest value is around 0.35Ω in the case of a run at 30°C (Figure 7), corresponding to optimal hydration of the fuel cell while the smallest one is around 0.42Ω at 45°C corresponding to a perpetual drying state.

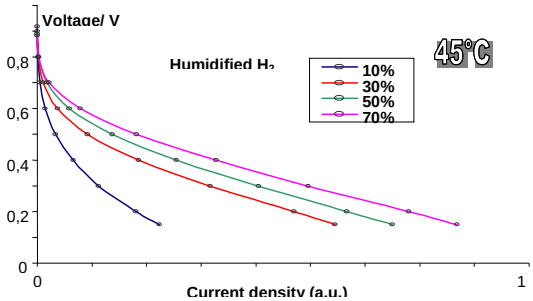

Figure 6. Polarization curves of a microfuel cell running with passive air-breathing system in different relative humidities. Humidified Hydrogen, T°=45°C.

Figure 7 demonstrates that internal resistance (equivalent to the membrane resistance at first approximation) is not only dependent on the relative humidity of the air but also on the running point, especially in the r.h. low range. When r.h. reaches around 50%, whatever the current density is, internal resistance is quite constant and optimal all over the considered voltage range. That means the environment is wet enough to ensure a good hydration of the membrane and of the composite catalyst layers, which contained Nafion® as a binder too.

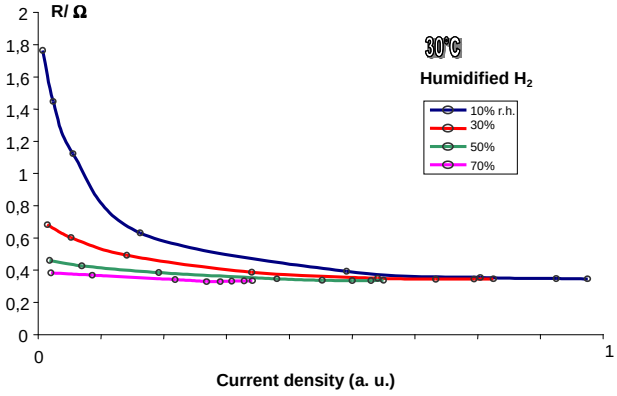

Figure 7. Internal resistance versus current density for a micro fuel cell running with passive air-breathing system in different relative himidities. Humidified Hydrogen, T°= 30°C.

By only playing with the geometry of the packaging, it has been possible to drastically improve the performances of the fuel cell at 45°C. The new packaging tended to decrease the evaporation

phenomenon at 45°C, which is favorable for power densities all over the r.h. range.

4. CONCLUSION

This study highlights that the running of the micro fuel cell is not easy to manage in passive air because of its dependence on the different external "interdependent" parameters quoted above (i.e. temperature, air humidity, dry or humidified hydrogen, packaging geometry).

Even if assembly of several micro fuel cells in series is dependent on these different parameters too,

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the prototype of Figure 8 makes it possible to supply more than 2 Watts in passive air-breathing conditions.

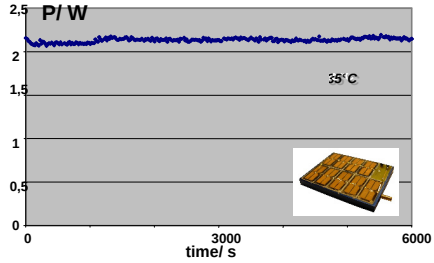

Figure 8. Evolution of the power density versus operating time of a prototype (potentiostatic mode).