# 3D ZINC-AIR MICROBATTERIES, GOING BEYOND LITHIUM-ION TECHNOLOGIES

Jérémy **Freixas**,
Thierry **Brousse** (Institute of Material Science Jean Rouxel, Nantes),
Christophe **Lethien** (Institute of Electronics, Microelectronics and Nanotechnologies, Lille)

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**Abstract** The studies presented in the frame of this thesis are focused on zinc-air battery miniaturization, an electrochemical energy storage system that shows a higher volumetric and gravimetric energy density than the lithium-ion technology, mostly investigated in literature. The micromachining of a silicon substrate allows designing a high specific surface scaffold: 3D geometrical gain enhances the properties of charge storage for the electrodes of the microbattery. 3D microstructures exhibiting various geometrical designs have been studied: for instance, silicon micro-tubes (4,2µm outer diameter) 109 µm-depth (60:1 aspect ratio) provide a specific surface to the footprint ratio close to 70. Then, this scaffold is coated by the active materials using conformal depositions methods. This process leads to a 3D zinc metallic anode (300nm-thick) exhibiting a surface capacity of 1mAh.cm$^{-2}$ in aqueous electrolyte (potassium hydroxide 0,7M). Cell voltage is 1,2V. For the first time in literature, a miniaturized air electrode has been manufactured, based on a porous microchannel network on the front side of silicon substrate, and the etching of a cavity on the back side. Once silicon wafer is micromachined, a platinum conformal thin film provides the conductive properties to the electrode while a manganese dioxide layer enhances the catalytic activity. This original concept of 3D air electrode presents a behavior similarly to a commercial one, but with a significant reduced size.

**Keywords** Zinc-air, Electrolytic deposits, 3D electrode, Bosch process

## 1- Introduction

The general goal of this thesis is to provide a sufficient energy storage density for small connected sensors. **Fig 1** show an example of such object: this optical sensor is as thick as a 1 cent coin.

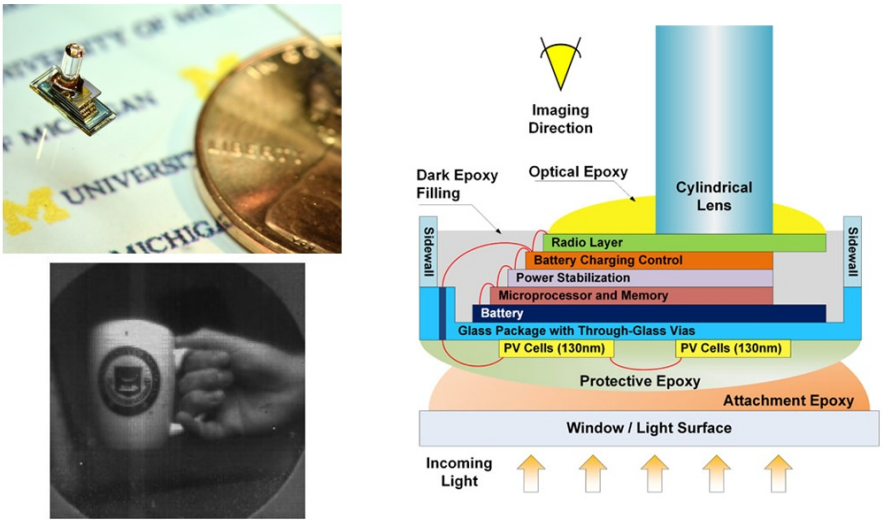


*Figure 1 – Michigan Micro Mote (Kim et al. 2014)*

Such objects show some characteristics:

- They are **compact**: so do need to be all the components used to build this system
- They are **mobile**: energy need to be harvest from the environment and stored
- They are **connected**: energy density need to be higher than 10mWh.cm$^{-2}$ (here, the surface measured is the footprint) to provide sufficient life battery
- They are manufactured with **microelectronics technologies**: the energy storage device need to be manufactured with the same technologies for a better integration in the system

Part of the solution to theses specifications: **microbatteries**!

Microbatteries are composed of a stack of thin layers (thickness < 1µm) of materials on a substrate. Like in a common battery, you have: two current collectors, two electrodes and an electrolyte. This is not a new concept: the first patent on microbatteries was registered in 1969. Some devices are already available in the market, but there are not denses enough to be embedded in small sensors.

That's why we identify two main enhancement strategies:

- Working on **electrode geometry** in order to have an higher interface surface
- Choosing other electrochemical redox couples than those involved in lithium-ion technologies to get higher energy density (= **metal-air**)

The first step consists in conquering the third dimension: the substrate is microstructured in order to have higher specific surface ($S_{3D}$) and low footprint ($S_{2D}$). **3D gain** is defined as the ratio of the total surface (orange + blue + green surfaces on **Fig 2**) of the electrode by the footprint (orange surface on **Fig 2**).

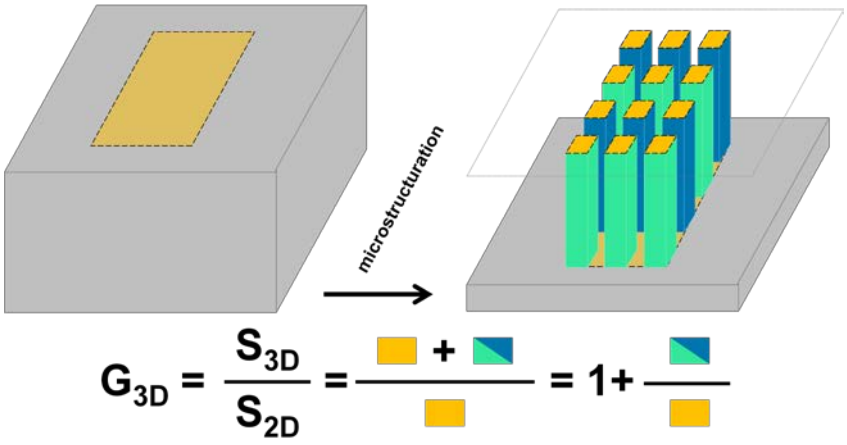


*Figure 2 – Substrate Microstructuration*

The second step consists in switching to a zinc-air battery. A zinc-air battery is composed of a metallic zinc anode, an alkaline electrolyte and an air cathode. The role of this air cathode is to make breathe the battery. As shown in **Fig 3**, oxygen is going through the gas diffusion layer. Then, the reaction can occur with the electrolyte. A catalyst is used to facilitate the reaction (kinetics are pretty poor without).

During discharge, zinc is oxidized and each atom frees 2 electrons. At the air cathode, electrons are taken by oxygen atoms. Global reaction occurs at 1.65V (practical tension: **1.1V-1.2V**).

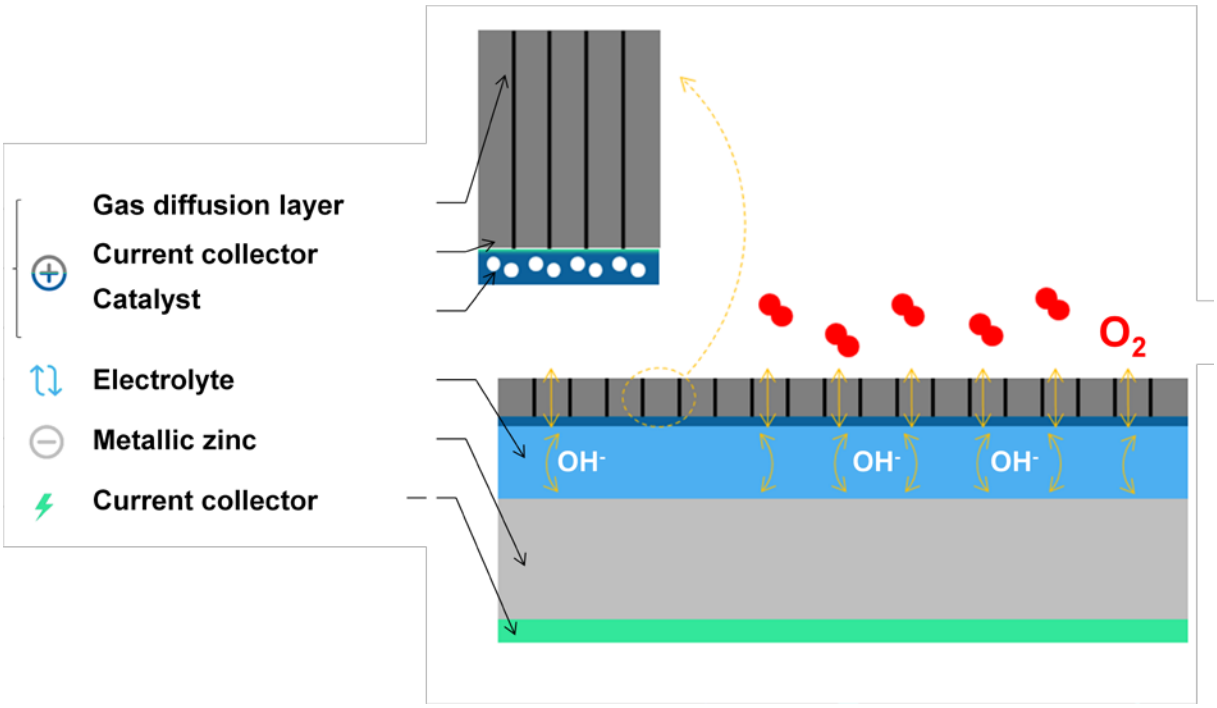


*Figure 3 – Zinc air battery*

Some studies are available in the literature about zinc-air battery miniaturization. But these works are not complete: electrolyte leakage, lost of structuration after the 1rst discharge, low 3D gain and use of commercial air cathode (which is too thick and hard to assemble with the 3D zinc anode) are still inhibiting the potential for the use of these microdevices.

This thesis aimed to achieve these goals:

- Designing a **whole architecture** for zinc-air batteries **compatible with microelectronics fabrication technologies**
- Providing a **3D scaffold** that will be **stable** during all the life of the battery

Our approach: micromachining a silicon substrate and then recover it with materials thanks to conformal deposit processes.

## 2- Methods

Bosch Process: **dry deep etching of silicon**.
Before processing, an etching mask is realized with **photolithography** techniques as shown in **Fig 4**.

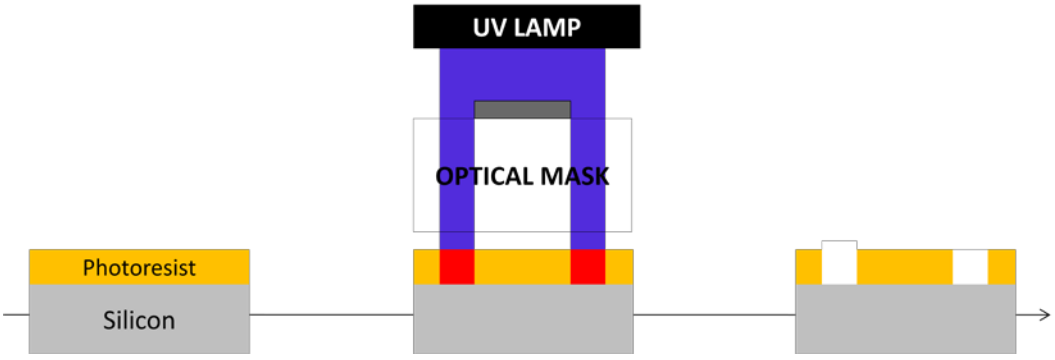


*Figure 4 – Photolithography*

Then, silicon is etched with 3-step Bosch Process (**Fig 5**). Bosch process is realized with the **repetition of 3 steps**:

- **Chemical etching** of silicon (which is isotropic)
- **Passivation** layer deposition (which will protect the lateral surface of microstructures)
- **Depassivation** step (which will remove the passivation layer by ionic sputtering in order to continue the etching of the silicon cavity)

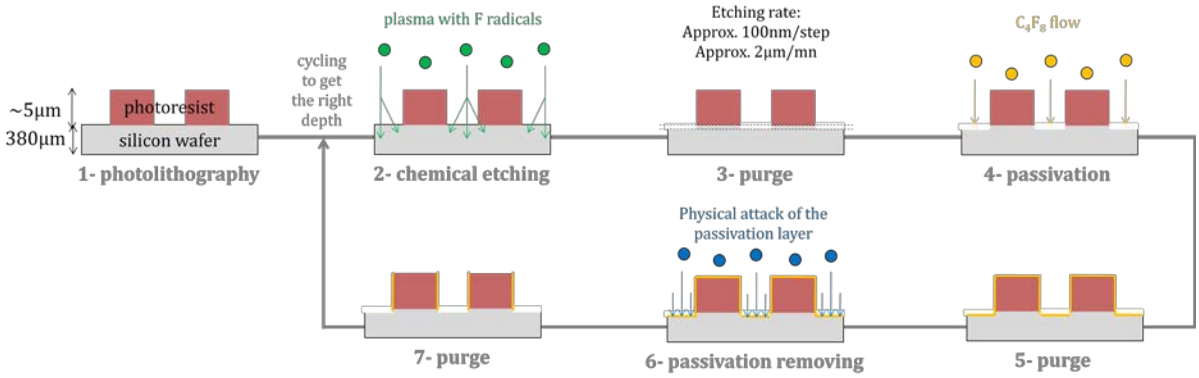


*Figure 5 – 3-steps Bosch process*

In order to have the right etching profile, one can play on:

- Reactor pressure
- Sample holder temperature
- Gas composition and flow
- Inductive coupled generator power (rules mainly the plasma density)
- Capacitive coupled generator power (rules mainly the ionic energy)

Once the substrate is microstructured, thin layers of material are deposited (**Fig 6**). Two processes are used in this work:

- **Atomic Layer Deposition** (ALD)
- Pulsed **electrolytic deposition** (3 electrodes system)

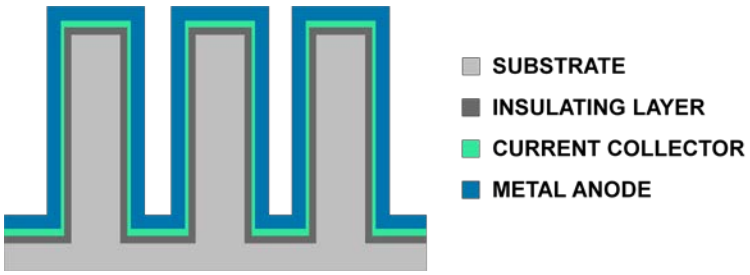


*Figure 6 – 3D electrode stack of materials*

## 3- 3D Anode

The work realized on the 3D anode is a good illustration of this approach.

First, the substrate is micromachined. Etienne Eustache and Christophe Lethien already developed some processes for “microtubes” (**Fig 7**).

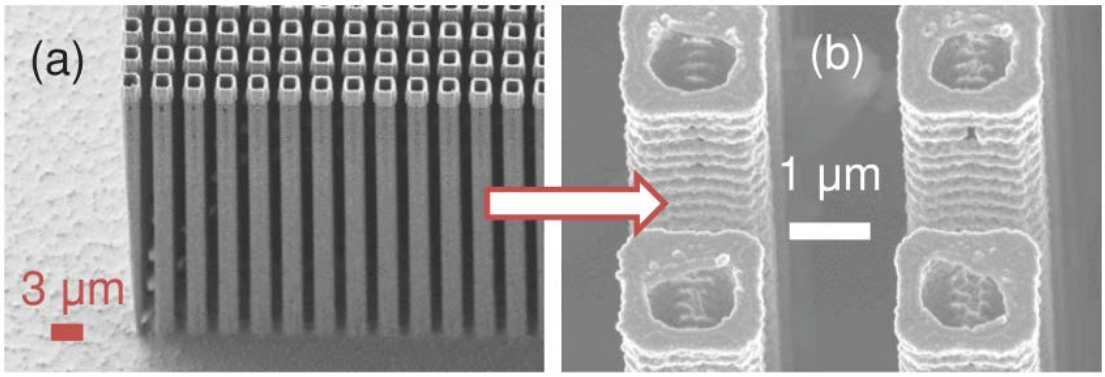


*Figure 7 – Microtubes (Eustache et al. 2014)*

During this thesis, the goal was to get **higher 3D gains**. To do so, we decided to design a progressive etching process. Indeed, if you keep constant values for all the settings (step time, plasma power, etc) during all the process, you can get either too thin structures (with poor mechanical properties) or too thick structures (with 'silicon grass' reducing the 3D surface).

Here, settings are updated every 100 cycles (**Fig 8**):

- Passivation time is progressively increased (in order to get a thicker passivation layer to protect better the lateral surface of 3D structures)
- Depassivation power is progressively increased (in order to remove more efficiently the passivation layer on horizontal surfaces)
- Chemical attack plasma power is progressively reduced (in order to keep walls vertical)

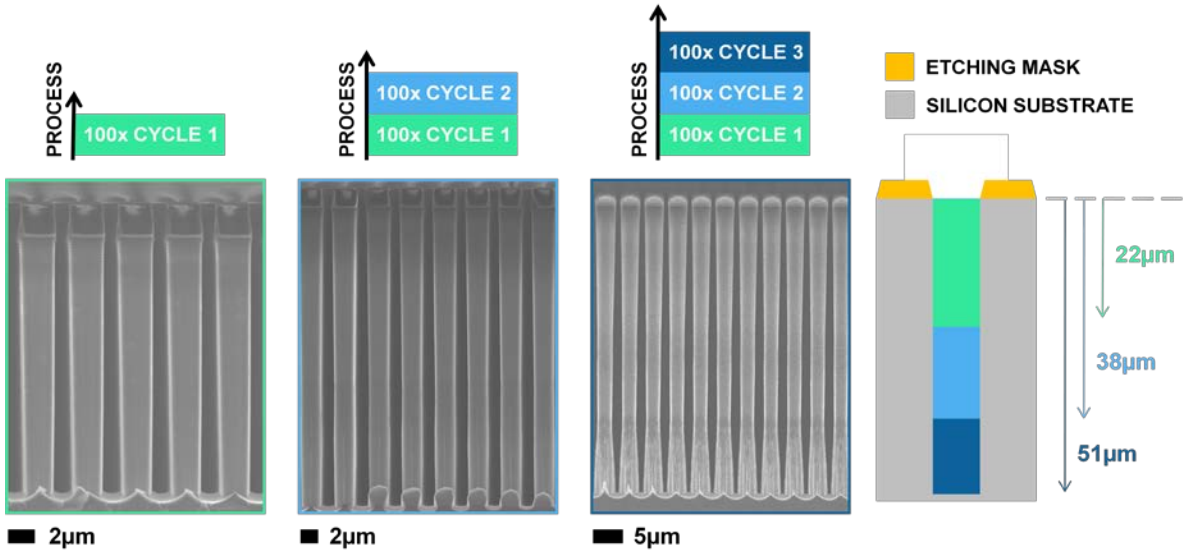


*Figure 8 – Etching process with 2 updates*

It is better but not perfect: the bottom of the microstructures is still a bit obstructed. In order to enhance the etching profile, depassivation time for cycle3 is increased. An angle of 89.7±0.2° is measured after this modification: microstructures are straighter. Then, by testing other settings (trial and error approach) we succeeded in reaching higher 3D gains. This was done too with other microstructure geometries: our record so far is a 3D gain of **70**, which is better than ones reported in the state of art (**Fig 9**). It means that if you take one squared piece of silicon of 1cm large by 1cm length recovered with these microstructures, you get 70cm² of specific surface.

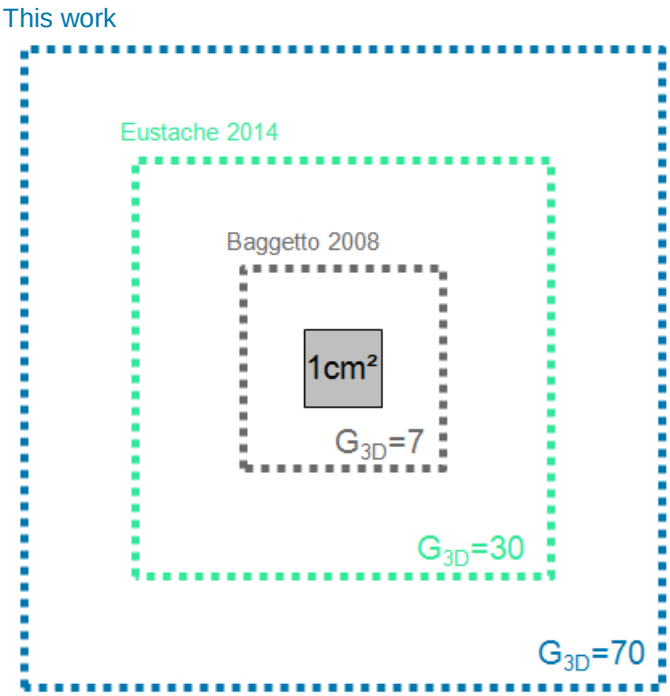


*Figure 9 – 3D Gain, state of art (Baggetto et al. 2008; Eustache et al. 2014)*

Then, materials are stacked on the microstructures:

- Alumina ($Al_2O_3$) as electronic insulating layer by ALD
- Platinum as current collector by ALD
- Zinc as electrode active material by pulsed electrolytic deposition

Zinc electrodeposit is not conformal: approximately 10% of the height of microstructures (on the top) is not recovered. Then, electrochemical characterizations are performed in order to quantify the specific capacity of the electrode. To do so, a flat cell is used (**Fig 10 a**).

A flat cell is composed of 3 pieces of PTFE (Teflon) assembled in a prototype of battery. The discharge profile obtained (**Fig 10 b**) is similar to one on literature: a discharge plateau around 1.1V-1.2V and a strong slope at the end of the reaction. On this configuration (3D Gain = 40, Zn layer thickness = 300nm, electrolyte = KOH 0.7M), the 3D electrode shows a capacity of **1mAh.cm$^{-2}$**.

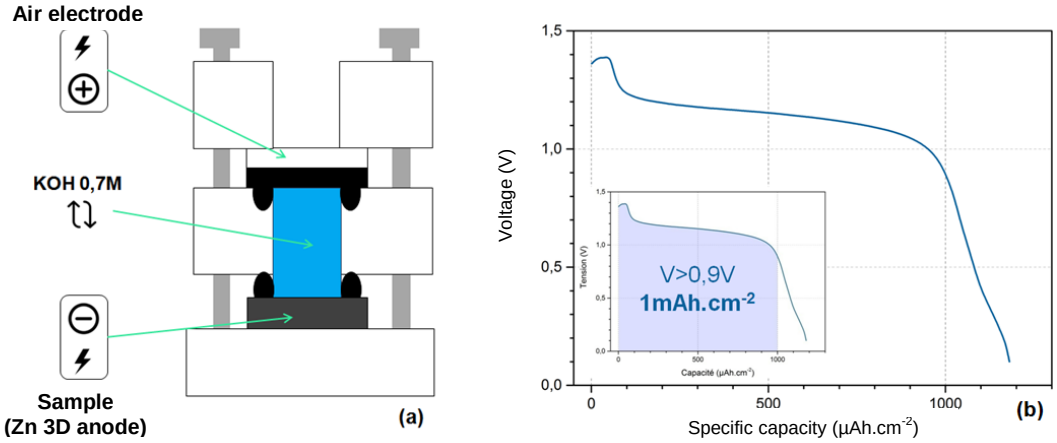


*Figure 10 – Electrochemical characterization*
*(a) Flat cell (b) Discharge curve*

The theoretical value is higher: 7mAh.cm$^{-2}$. To explain this difference, post-discharge analysis of the electrode was performed (**Fig 11**).

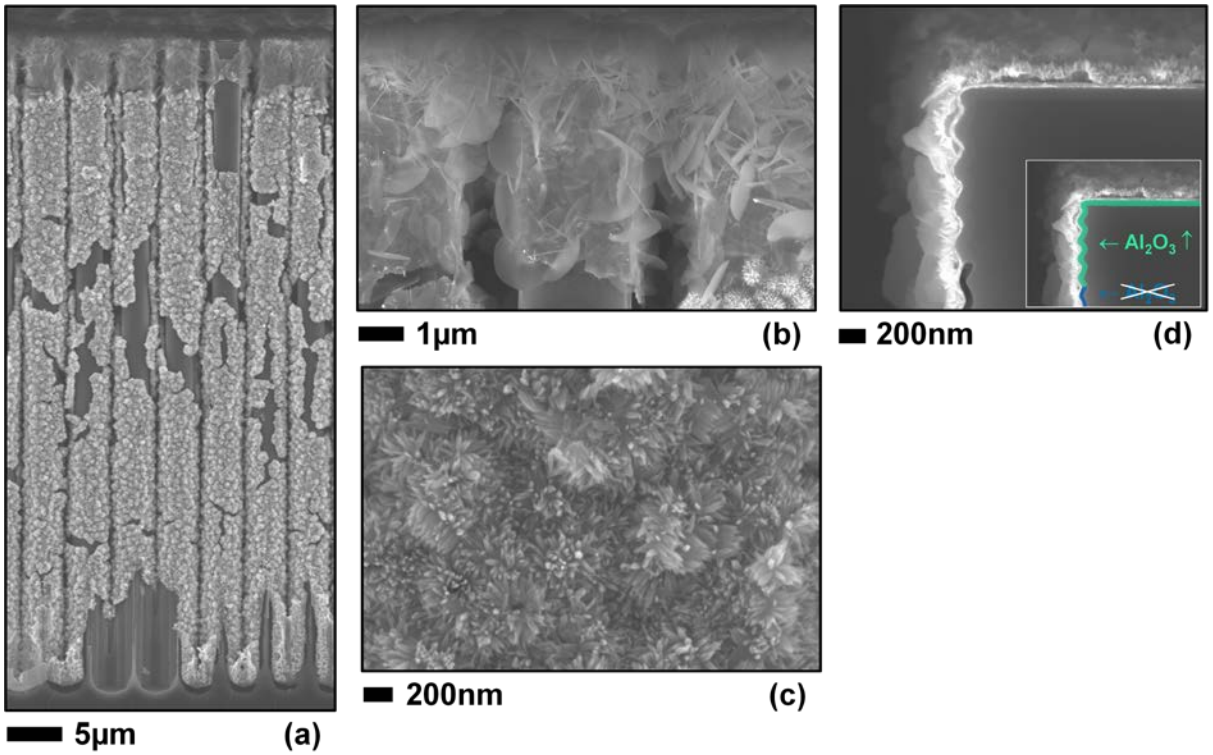


*Figure 11 – Post discharge analysis of the 3D anode*

As shown in **Fig 11 a**, the stack seems to be attacked during the discharge of the anode. A material has precipitated on the top of structures (**Fig 11 b**) and the morphology of the zinc layer has changed (**Fig 11 c**). Alumina layer seems to be etched (**Fig 11 d**): KOH solution is known to be an efficient etchant of $Al_2O_3$, but these two chemicals are not supposed to be in contact in the battery.

To have more insights, EDX analysis was performed. Aluminum is not detected is the area were the zinc was electroplated. But, aluminum is still detected on the top of microstructures after discharge. A phenomenon seems to occur during zinc electroplating: zinc could diffuse into the platinum layer. During discharge, zinc is oxidized: that can generate some porosity into the platinum layer. Alumina layer is then etched, and the platinum layer loses his support. This could explain the difference between theoretical and practical capacity of the electrode: the electrode is not fully discharged.

Changing the material used as the current collector layer could enable a proper characterization of the electrode. Compared to literature, values obtained for specific capacity and energy density are in the same order of magnitude as the one found in literature (Fu et al. 2006; Chamran et al. 2007; Armutlulu et al. 2011). The goal of 10mWh.cm$^{-2}$ can be reached if this issue of current collector is resolved, and if the overall surface deployed by 3D structuration is recovered by a zinc layer.

## 4- Air cathode

Similar approach was realized for the design of a porous air electrode. Here, the reaction mechanism involving oxygen is completely different, so do is the microstructures geometry. As shown in **Fig 12**, on the top face of the silicon substrate, channels are micromachined to enable gas diffusion into the battery. On the bottom face of the silicon substrate, a large cavity enables the contact of the oxygen

and the electrolyte. This device is also manufactured thanks to Bosch Process (and photolithography).

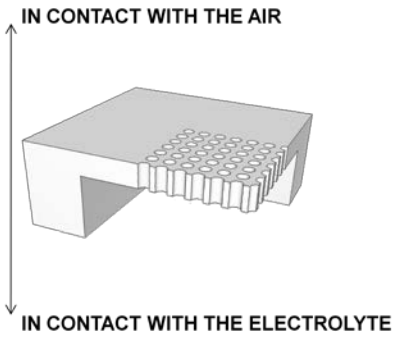


*Figure 12 – Microstructures for the air electrode*

Once the substrate microstructured, thin layers of materials are stacked:

- Alumina ($Al_2O_3$) as insulating layer
- Platinum as current collector
- Manganese dioxide as catalyst for the oxygen reactions

Conformal deposit of $MnO_2$ is performed with pulsed electroplating method. The optimization of the process is done on microtubes. The morphology of the deposit obtained opens the way for an higher specific surface and an augmentation of catalytic sites. Such method is then reproduced on the air electrode silicon scaffold. $MnO_2$ deposit is less visible: it has been decided to perform nanoparticles deposition to ensure a good electrical contact. The presence of these particles is confirmed by:

- Raman spectroscopy: shifts of gamma phase of $MnO_2$ are noted.
- Electrochemical characterization: catalytic activity of the electrode is higher (by a factor 14) after $MnO_2$ deposition. This analysis shows the benefits for the catalytic activity of the air electrode.

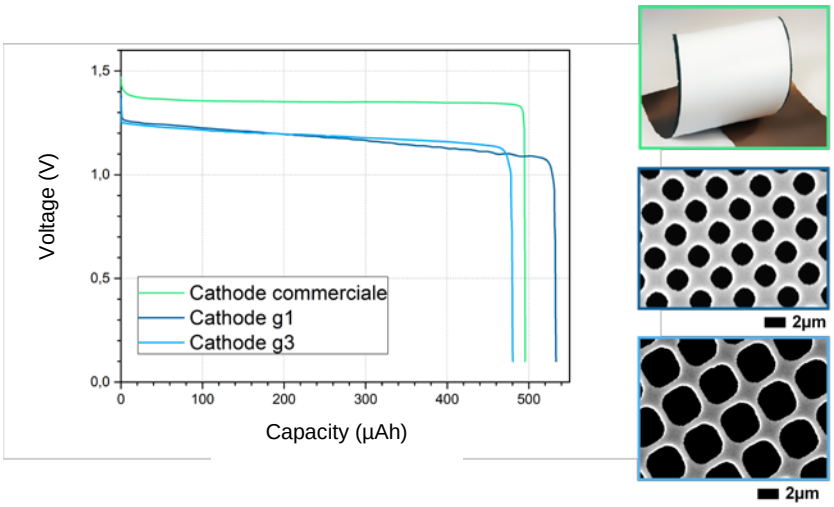


*Figure 13 – Commercial air-electrode vs Silicon-based air-electrode*

Zinc-air batteries are assembled in order to compare a commercial air cathode (green curve on **Fig 13**) and silicon-based one (blue curves on **Fig 13**). The zinc anode is not microstructured in this configuration.

For all electrodes, a discharge plateau is observed, finishing by a vertical slope. The three batteries were discharged when the anode was fully oxidized: this is the reason why the capacity is quite similar from one to another. Our micromachined electrodes seem functional, even if they are not optimized: voltage cell is lower, due to polarization.

Another parameter has been quantified: evaporation rate of water through the electrode. This parameter is really important when an aqueous electrolyte is used. To do so, an hermetically sealed cell is filled with a KOH solution. By temporal monitoring of the variation of the weight of this cell, we can estimate the evaporation rate through the electrode: 24mg.h$^{-1}$ for a commercial one and 6mg.h$^{-1}$ for a silicon based one. We can then foresee that a microbattery assembled with a micromachined electrode can work longer than a microbattery equipped with a commercial one.

## 5- Conclusion and perspectives

This work leads to a new architecture for zinc-air microbatteries (**Fig 14**). This silicon scaffold is then recovered by conformal deposits of materials. Electrochemical characterizations were performed: electrodes present a behavior similar to commercial one, even if the fabrication process needs to be optimized.

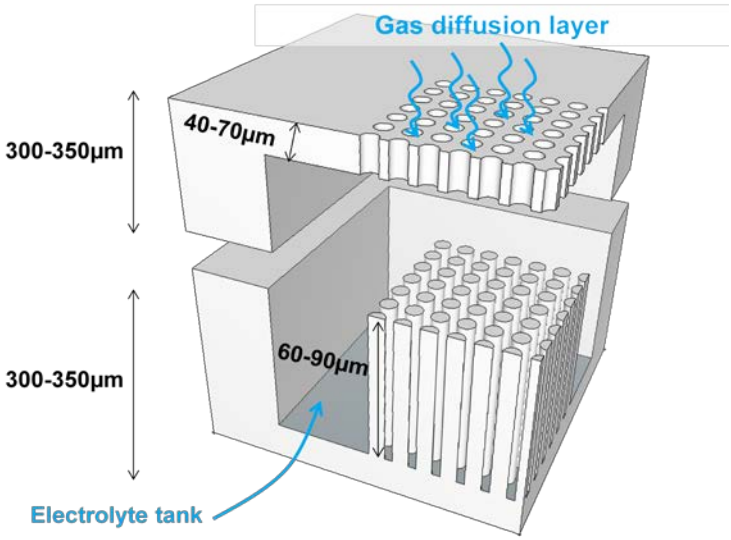


*Figure 14 – Full architecture for a micromachined zinc-air microbattery*

In order to go further, some actions have been identified:

- Get higher 3D gain thanks to hierarchical porosity in electrodes
- Developing conformal deposits methods for other materials: transition metal nitrides like titanium nitride or vanadium nitride (current collector), aluminum (anode), cobalt oxide (air electrode catalyst)
- Characterization of a full micromachined battery
- Developing an all solid state device, thinking about assembling step
- Study of the ageing of the microbattery (in use or in shelf)

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Thanks for your attention ☺

## References


**Armutlulu**, Fang, Kim, Ji, Bidstrup et Allen, **2011**, A MEMS-enabled 3D zinc–air microbattery with improved discharge characteristics based on a multilayer metallic substructure, *Journal of Micromechanics and Microengineering* 21 (10), 104011

**Baggetto**, Niessen, Roozeboom et Notten, **2008**, High Energy Density All-Solid-State Batteries: A Challenging Concept Towards 3D Integration, *Advanced Functional Materials* 18 (7), 1057‑66

**Chamran**, Min, Dunn et Kim, **2007**, Zinc-air microbattery with electrode array of zinc microposts, In *IEEE MEMS 2007*, 871‑74

**Eustache**, Tilmant, Morgenroth, Roussel, Patriarche, Troadec, Rolland, Brousse et Lethien, **2014**, Silicon-Microtube Scaffold Decorated with Anatase TiO2 as a Negative Electrode for a 3D Litium-Ion Microbattery, *Advanced Energy Materials* 4 (8), 1301612

**Fu**, Luo, Huber et Lu, **2006**, Design and Fabrication of a Micro Zinc/Air Battery, *Journal of Physics: Conference Series* 34 (1): 800

**Kim**, Lee, Foo, Pannuto, Kuo, Kempke, Ghaed, Bang, Lee, Kim, Jeong, Dutta, Sylvester et Blaauw, **2014**, A millimeter-scale wireless imaging system with continuous motion detection and energy harvesting, in *2014 Symposium on VLSI Circuits Digest of Technical Papers*, 1‑2