

# Fabrication of 3D carbon microelectrodes for Li-Ion battery applications

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## ABSTRACT

The fabrication of very high-aspect ratio 3D carbon microelectrodes for Li-Ion batteries is presented. Using a pyrolysis process under inert conditions, thick layers of patterned SU-8 photoresist (up to 600  $\mu\text{m}$  in height) are converted into carbon. The micro-structures resulting from this process are used as anode for a Li-Ion battery. A detailed explanation on how to create SU-8 structures of aspect ratios as high as 15:1 using UV light is provided. New shapes that are more mechanically stable during the pyrolysis shrinkage are introduced. Some insight into how to create these structures on top of copper foil used as a current collector is provided as well.

**Keywords:** SU-8, C-MEMS, 3D microbatteries,

## 1 INTRODUCTION

The rechargeable lithium-ion battery is one of a number of new battery technologies that have been developed in the last ten to fifteen years. This type of battery, operating at room temperatures, offers several advantages compared to conventional aqueous battery technologies, like a higher energy density (up to 135Wh/kg, 300 Wh/L), higher cell voltage (up to 3.7V), longer shelf life (5-10 years) and extended cycle life (1000 to 3000 cycles). Lithium-ion batteries are presently the most widely used rechargeable power sources for consumer electronics.

Highly ordered graphite as well as hard and soft carbons are used extensively as the negative electrodes for commercial Li-ion batteries. For small microbatteries, with applications in miniature portable devices, the achievable power and energy densities do not scale down favorably because packaging and internal battery hardware determine the overall size and mass of the completed battery to a large extent. One approach to overcome the size and energy deficiencies of 2D microbatteries is to develop 3D battery architectures based on specially designed arrays composed of high aspect ratio 3D electrode elements.

Our work on carbon-micro-electromechanical systems (C-MEMS) suggests that they might provide an interesting material and a microfabrication solution to the battery miniaturization problem.

## 2 MICROELECTRODE FABRICATION

The main idea behind the C-MEMS processing technology is the pyrolysis of previously patterned photoresist precursors. By doing this, it is possible to achieve high dimensional control over carbon structures that otherwise would be very difficult (if not impossible) to fabricate using traditional manufacturing techniques.

The steps involved in the fabrication of the microelectrodes are the patterning of the photoresist and then the pyrolysis of it inside a furnace under inert conditions (see Figure 1).

### 2.1 SU-8 processing

In order to achieve truly high aspect ratio 3D structures, we need to use a type of photoresist that can be deposited at heights up to 600  $\mu\text{m}$ . The use of the SU-8 negative tone photoresist from MicroChem<sup>®</sup> allows us to do so.

We begin spin coating the photoresist (SU-8(100) formulation) at 500 rpm for 35 seconds on top of 4 inch diameter 5000 $\text{\AA}$  SiO<sub>2</sub>/Si wafers using a Laurell photoresist spinner.

Before patterning the photoresist, it is necessary to do a soft bake of it. In this step, the solvent of the photoresist is evaporated and only the monomer remains. The silicon substrate with the spin coated photoresist on top is placed in a leveled hotplate. The temperature cycle for this process is: from room temperature (21°C) to 96°C at a rate of 150°C/h; hold at 96°C for 10h; turn off the hot plate and let it cool down. For the exposure, the dose is 3500 mJ/cm<sup>2</sup> at an intensity of 5.8 mW/cm<sup>2</sup> for a thickness of 600  $\mu\text{m}$ . To expose the photoresist, we use an intermittent process because otherwise the heat of the UV lamp melts the photoresist and it gets attached to the mask.

After the exposure, the post exposure bake takes place for 25 minutes at 90°C in the same leveled hot plate.

Development is carried using a SU-8 developer from MicroChem<sup>®</sup> (NANO<sup>™</sup> SU-8 Developer) until the structures are completely released.

### 2.2 Pyrolysis process

Photoresist-derived C-MEMS architectures are obtained in a two-step pyrolysis process in an open end quartz-tube

furnace. The samples are post-baked in a  $N_2$  atmosphere at  $300^\circ C$  for about 40 min first, then heated in  $N_2$  atmosphere with 2000 standard cubic centimeter per minute (sccm) flow rate up to the desired temperature (around  $900^\circ C$ ). The atmosphere is then changed to forming gas [ $H_2$  (5%)/ $N_2$ ] flowing at a rate of about 2000 sccm. The sample is kept at  $900^\circ C$  for one hour and then the heater is turned off and the samples are cooled in  $N_2$  atmosphere to room temperature. The heating rate is about  $10^\circ C/min$ .

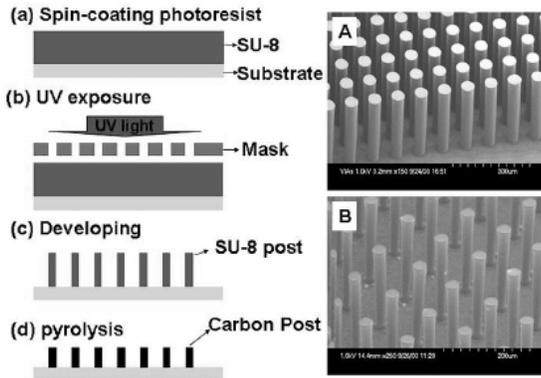


Figure 1: A schematic drawing of the C-MEMS process and typical SEM photos (A) before and (B) after pyrolysis

### 3 ELECTRODE GEOMETRIES

The main challenge when fabricating high-aspect ratio carbon microelectrodes is to have a perfect array of them. This is one of the main constraints in the design because a contact between electrodes creates a shunt that completely ruins the normal operation of the battery.

The most critical step of the fabrication is the developing process. The difficulty comes from the fact that the surface tension of the solvent used (1-Methoxy-2-propyl acetate) tends to aggregate the electrodes. There is another fact that amplifies this effect: since the SU-8 is a negative tone photoresist, the monomers crosslink at the locations where there is incident light. Since the thickness of the photoresist we are working with is around  $600\mu m$ , it is difficult for the light to arrive at the very bottom of the photoresist layer, resulting in shapes that have a base thinner than the top (see figure 3A).

Capillary forces result from trapped liquid that, due to Laplace pressure differences and surfaces tension forces, produce an attractive force. In our case, the presence of the liquid is a byproduct of the release process (developing process). While the capillary forces themselves are enough to cause sticking, an additional problem arises when the liquid starts to evaporate. The volume reduction as the liquid evaporates can produce enough force to collapse fragile suspended structures (like our SU-8 cylinders).

This problem has been analyzed using a Finite Elements Method program (FEMLAB by Comsol®), and the simulation results fit properly with the experimental results:

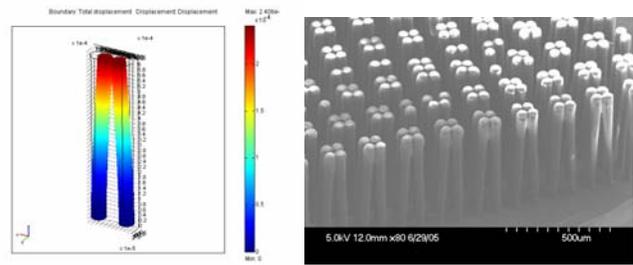
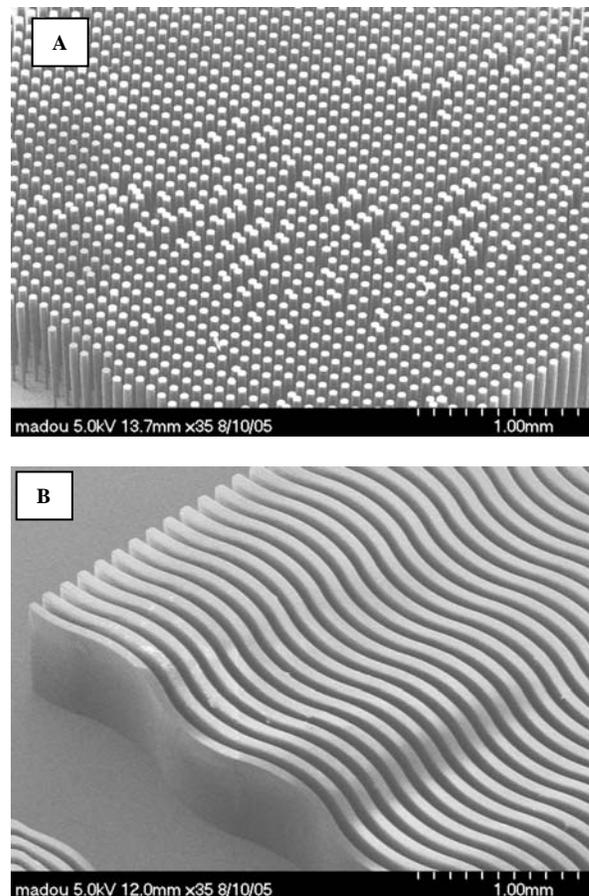


Figure 2: Simulation and reality of the aggregation effect after the developing step in the fabrication process.

In order to overcome this problem, we have developed new geometries that have a higher momentum of inertia than the circular shapes. The two new designs considered are called "waves" and "Z" shapes.

Comparing the new designs with the cylindrical ones, we can see that the new ones are clearly superior in terms of uniformity and regularity. To compare them, the feature sizes are the same. In the case of the shown pictures, the diameter of the cylinders is  $50\mu m$  at the top, and the thickness of the walls and the Z's is also  $50\mu m$ .



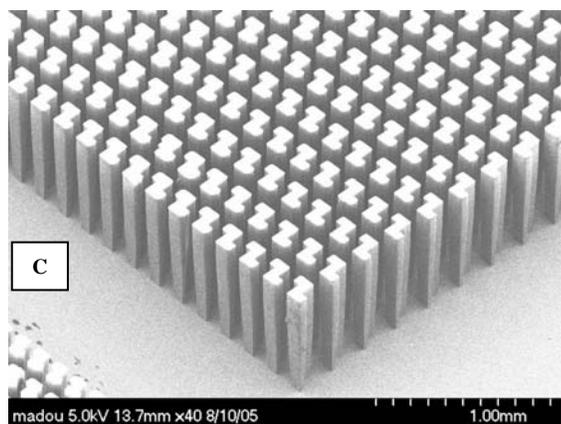


Figure 3: The newly proposed designs (figures 3B and 3C) show a superior mechanical strength during the developing process. All these structures are made over the same substrate and thus have been under the same fabrication conditions.

Not only is the mechanical strength improved, but also the surface area of the entire system. This is another crucial design parameter since the Li-ion intercalation process is a surface driven process. The more surface of carbon there is, the more lithium is going to be intercalated.

Making the supposition of smooth surfaces and that the features are 40 $\mu\text{m}$  thick and a gap between features of 40 $\mu\text{m}$ , the total surface area present in 1  $\text{cm}^2$  of these designs as a function of the height is presented in the following table:

( $\text{cm}^2$ )	Cylinders	Z's	Walls
100 $\mu\text{m}$	2.96	3.50	3.51
300 $\mu\text{m}$	6.89	8.50	8.53
600 $\mu\text{m}$	12.78	16.00	16.06

Table 1: Total surface area per  $\text{cm}^2$  footprint as a function of the type and the height of the different designs.

Once converted into carbon after the pyrolysis process, these designs look as shown in the pictures below:

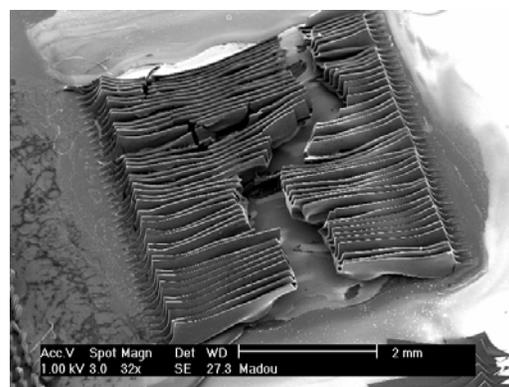
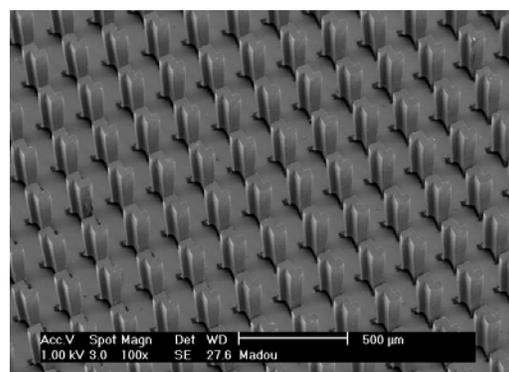
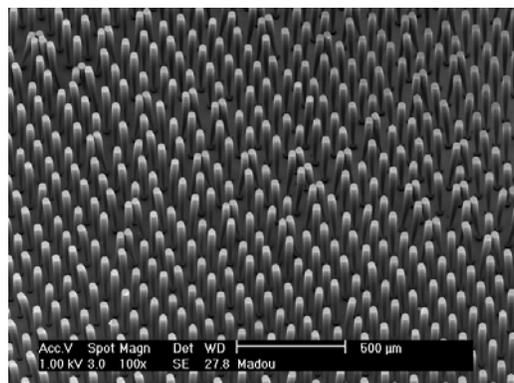


Figure 4: The new geometries after pyrolysis. Note the uniformity of the Z's array compared to the cylinders one.

Due to the shrinkage during the pyrolysis process, the structures change in shape isometrically. Since the walls are bigger continuous structures, the shrinkage makes them collapse completely. Therefore, this design has to be discarded as a microelectrode for a battery.

## 4 SUBSTRATE

In a Li-ion battery, it is very important to ensure that the electrons that come out from the lithium intercalation process can move out from the battery. Since the ohmic losses inside the electrodes are very difficult to eliminate (because they arise from the same materials property), it is important to minimize the losses during the transport of electrons once they are out of the electrode. That is the function of the current collector.

The first C-MEMS designs had been fabricated over silicon wafers to ensure the feasibility of the concept, but once it has been proved, the selection of a good current collector for battery applications is a must.

In commercial Li-ion batteries, the most common current collector for the anode is a copper foil. For that reason we have also developed a method for building the C-MEMS structures on top of copper foils. The substrate used in our case is 25  $\mu\text{m}$  thick, 99.8% pure, cold rolled copper foil provided by Alfa Aesar<sup>®</sup>. The process used to create the C-MEMS structures is the same one described in section 2.

The main obstacle in using copper foil instead of silicon wafers appears during the pyrolysis process because Cu foil has a very different Coefficient of Thermal Expansion (CTE) compared to carbon:

( $10^{-6} / ^\circ\text{C}$ )	<b>C</b>	<b>Si</b>	<b>Cu</b>
Coefficient of thermal expansion	0.25	2.9	16.7

Table 2: Coefficient of Thermal Expansion for carbon and the two substrates used: silicon and copper.

The bigger the difference between the CTE of the carbon and the substrate, the more difficult it is to ensure the adhesion between them. In general, small features will be less prone to detach from the substrate. It is possible to observe this effect in the picture below: The thin SU-8 layer that surrounds some of the structures breaks during pyrolysis:

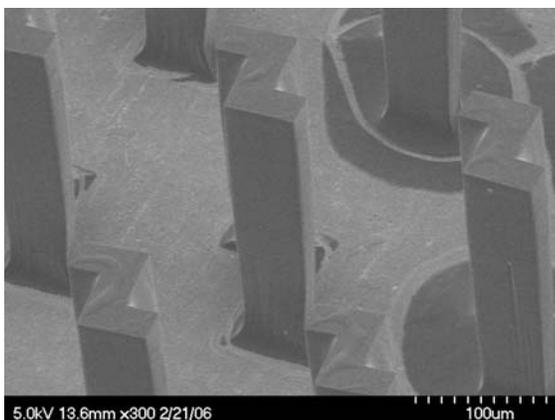


Figure 5: Z patterns over copper foil. Note the fissures surrounding the carbon structures.

The patterning of C-MEMS structures on top of copper foil has been proven.

It is important to observe that the spacing in between the carbon shapes has to be covered with carbon too, in order to increase the volumetric capacity of the proposed battery design. This issue will be tackled in future research.

## 5 CONCLUSIONS

The fabrication of very high-aspect ratio 3D carbon microelectrodes for Li-Ion batteries applications has been proven. The process with which thick layers of patterned SU-8 photoresist (up to 600  $\mu\text{m}$  in height) are converted into carbon has been explained. New shapes that are more mechanically stable during the pyrolysis shrinkage have also been presented. Finally, a discussion on the mechanical interaction between those structures and copper foil used as a current collector has been presented.

## ACKNOWLEDGEMENTS

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