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# Fabrication of Activated Carbon Electrodes by Inkjet Deposition

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## Abstract

*The inkjet deposition technology turns out to be interesting in various applications when one attempts to reduce manufacturing costs, simplify technological steps, and implement materials that could not be deposited in any other way. One of the limitations however, is the issue raised by resolution which is directly linked to the ejection head manufacturing technology. In this paper, a method of activated carbon deposition based on inkjet is presented. Activated carbon is extensively used in chemistry for its impurity absorption capabilities and in other applications like the fabrication of supercapacitors. It is shown in particular that by using a localized surface treatment with OTS and an activated carbon suspension stabilized by a surfactant, one can get 10  $\mu\text{m}$  structures, which are, therefore, much smaller than the ejection head nozzle diameter. To implement and optimize the process, the contact angle measurement technique is utilized.*

## 1. Introduction

With its high porosity, activated carbon is used as the electrode material for supercapacitors [1]. Standard assembly of supercapacitors is based on stacking up solid active material layers (activated carbon) with a separator between two collectors ("coin cell" package). The resulting coin cell device features a diameter of a few centimetres. The fabrication of miniaturised supercapacitors integrated on silicon substrate is of great interest in diverse microsystems applications that require energy storage. The integrated supercapacitor design that is proposed is then composed of interdigitated fingers (collectors) on which the active material has to be deposited. However, the deposition of activated carbon on the gold electrodes is a real challenge. In this work, the deposition of activated carbon was investigated through use of the inkjet

technique developed for polymers, oxides, metals and nanoparticles [2, 3, 4, 5, 6]. So far, no study of the deposition of activated carbon based on inkjet has been reported for grain sizes between 1 $\mu\text{m}$  and 10 $\mu\text{m}$ . To be able to use this method, a suspension that remains stable over time is required. This suspension will consist of an ink obtained by mixing activated carbon (AC) in ethylene glycol solution (carrying fluid), polytetrafluoroethylene (PTFE) which provides a mechanical link between the carbon particles in the substrate [3] and a surfactant, Triton X100 (p-(1,3,3-tetramethylbutyl) phenoxy-poly(ethylene glycol)) which contributes to the wettability and stability of the emulsion. The aim is first to obtain a stable AC suspension as a function of the surfactant concentration, and then to project this ink onto a gold electrode which is more hydrophilic than the surrounding hydrophobic silica surface. Hydrophobic silica was obtained by means of an octadecyltrichlorosilane (OTS) treatment aiming to concentrate the ink onto hydrophilic zones with a high surface energy that is, onto the gold electrodes. Through evaporation of ethylene glycol, one gets an activated carbon deposition located exclusively on the metal electrode.

## 2. Materials and means

To form the ink, a ethylene glycol solution from Sigma Aldrich was used to mix an alcoholic PTFE nanoparticle suspension from DuPont, with a Triton X100 surfactant from Sigma Aldrich and activated carbon from Kuraray Chemical Co. The OTS was provided by Sigma Aldrich. To measure the contact angle, a Digidrop machine was used while ink deposition was achieved with an Altadrop machine from Altatech Semiconductor. This is an automatic machine cassette to cassette equipped with a single nozzle head. Substrate temperature can reach 150°C. The temperature of the ejection heads can be adjusted

up to 120°C. Thanks to a special trombosopic system on the machine, the droplet formation and production rate could be controlled. Also, a movie camera was used to display the deposition and to align the drop on the pattern.

### 3. Ink and surface preparation

#### 3.1 Ink preparation

Suspensions were prepared by mixing first in ethylene glycol the Triton X100 with PTFE. The activated carbon was added afterwards [7]. The percentage of PTFE was 5 wt% of the activated carbon Weigth. This suspension was agitated for 12 hrs and placed in a test tube. The suspension behaviour was observed over time. Solutions featuring Triton compositions from 0.0001% to 5% were used. The AC composition was set to 3% weight relative to ethylene glycol. Higher concentrations yielded inks that were extremely difficult to jet.

#### 3.2 Surface preparation

Silicon dioxide (1500Å) was first grown on silicon wafer by thermal oxidation followed by the evaporation of 150 Å of chromium and 3000Å of gold. The electrodes patterns on which activated carbon had to be fixed were formed by photolithography and etching of the chromium/gold layer. Pattern widths varied from 50µm to 10µm. On the silicon wafer, zones were defined to make contact angle measurements on the metal or on the oxide.

The silicon dioxide or glass hydrophobic treatment has been extensively reported in the literature [8]. Following cleaning in a sulfochromic solution (2min), samples were soaked into an activation solution with 50% methanol and hydrochloric acid. After drying under nitrogen, samples were dipped for 30 min into an OTS solution diluted 2% in trichloroethylene. To get rid of the remaining solvent and OTS, acetone and deionised water were used.

### 4. Results and discussion

Ethylene glycol is a fluid that can easily be projected by inkjet. Its viscosity is 19.86mP.s at 20°C and can equally be reduced by rising temperature. With a boiling temperature at 200°C, depositions can be achieved at ambient temperature and the behaviour of the droplets deposited on the surface can be observed.

At 140°C, rapid evaporation was achieved and AC deposition was almost instantaneous.

#### 4.1 Variation of the contact angle and of the ink stability as a function of Triton X100 concentration

The curves in figure 1 show that the contact angle of a suspension on SiO<sub>2</sub> or on Au starts to decrease with a 0.5% Triton concentration and stabilizes from 2% onwards. With respect to sedimentation, three situations may

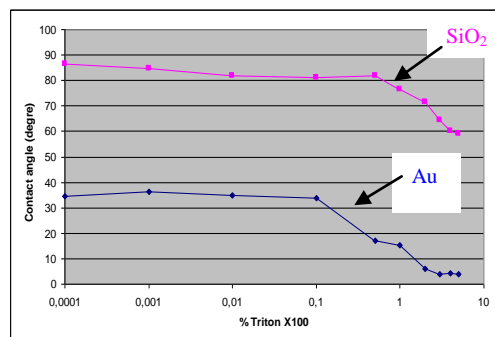
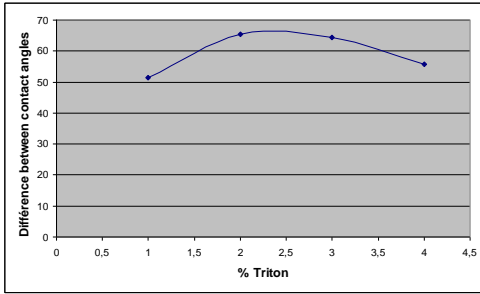


Figure 1 Contact angle variation on Au and SiO<sub>2</sub> versus % Triton X100 weight.

develop according to the Triton concentration after storage 48 hrs.

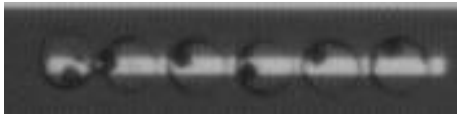
- from 0.0001 % to 0.01% Triton, three phases can be observed: an upper phase (transparent) ; a lower phase (opaque) and a carbon precipitation at the bottom of the test tube;
- from 0.01 to 1% Triton, two phases can be seen: an upper phase (opaque) with numerous particles in suspension and deposition at the bottom of the test tube;
- above 1%, there is only one phase in suspension.

It follows from these findings that only with a percentage in excess of 1% can a suspension be used. At lower concentrations, the precipitation of the ink storage tank can only cause clogging of the ejection head. The curve of figure 2 shows that the difference in contact angles for gold and silica is highest between 1 and 3% Triton, thereby facilitating a selective deposition of the ink droplet on the gold electrode. The surface energy



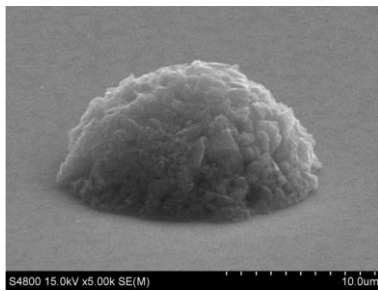
**Figure 2** Difference in contact angles for gold and silicon dioxide versus Triton X100 % concentration.

between gold and the ink tends to attract the ink droplet. If the contact angles on Au and on SiO<sub>2</sub> are too small and/or if the difference of contact angles between these two surfaces is too small, the ink droplet will remain in its original position after impact with the surface. As seen in figure 3 with 30° angles on Au and SiO<sub>2</sub>, a denser activated carbon particle distribution appears on the electrode edges. This phenomenon is also referred to as ‘the cup of coffee effect’ [9].



**Figure 3** Image with 30° contact angles on Au and SiO<sub>2</sub>.

If the ink droplet is projected outside the pattern onto a surface with a high contact angle, one gets, after ethylene glycol evaporation, a mound as shown in figure 4.



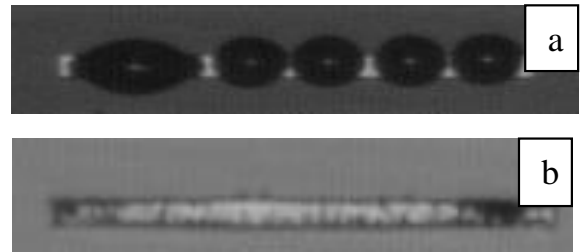
**Figure 4** CA deposition onto a high contact angle surface of SiO<sub>2</sub>.

#### 4.2 Importance of substrate temperature

Given the high boiling point of ethylene glycol, one can observe the deposition behaviour at room temperature and then have the ethylene glycol evaporated by a hot plate bake. The results can then be compared to a deposition where the substrate is heated at 140°C so as to cause an almost instantaneous evaporation of the droplets during impact on the surface. These operations were achieved with an ink containing 3% of activated carbon, 3% Triton, and 5% PTFE.

##### 4.2.1 Deposition at room temperature

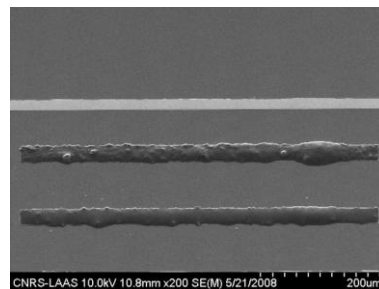
Figure 5 shows six ink droplets deposited at room temperature on a 50µm diameter nozzle on a 40µm wide and 650µm long electrode. Clusters of droplets bigger than the 40µm gold line can be observed. This could be a drawback for the case of interdigitated electrodes (risks of short-circuits). As ethylene glycol evaporation takes place, one can see that the droplets were joining up figure 5 (b) leading to a relatively inhomogeneous AC particle distribution.



**Figure 5** a) Droplets after inkjet printing at room temperature; b) AC dispersion after hot plate bake.

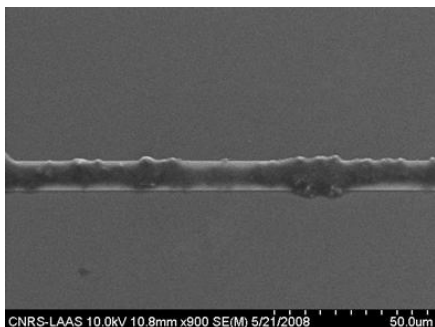
##### 4.2.2 Deposition at 140°C

A homogeneous deposition on the gold electrodes was obtained at 140°C by varying the density of the droplets.



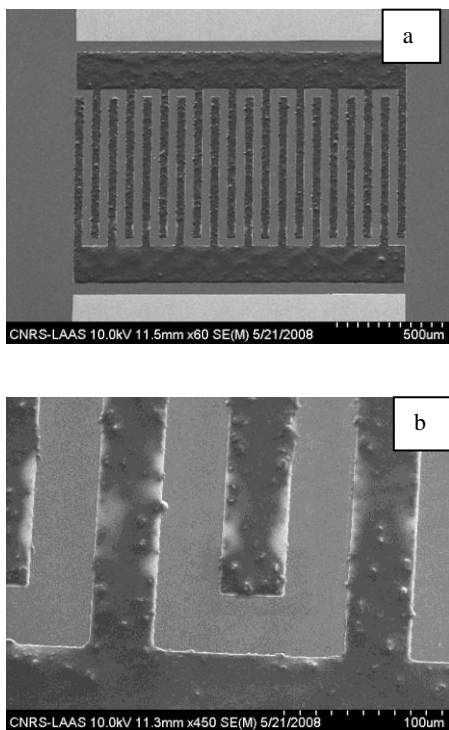
**Figure 6** SEM of 30µm wide electrodes.

This was achieved by increasing the number of passes or increasing the number of droplets. Patterns similar to those of figure 6 were obtained on a 30 $\mu\text{m}$  wide electrode. This approach was selected for 10  $\mu\text{m}$  wide electrodes as shown in figure 7. The main particles originate from the heterogeneous AC distribution with grain size of 10 $\mu\text{m}$ .



**Figure. 7 SEM of 10 $\mu\text{m}$  wide electrode.**

Figure 8 depicts an interdigitated electrodes structure



**Figure. 8 SEM of an interdigitated structure. a) general view; b) detail of the structure.**

with a spacing of 40 $\mu\text{m}$  between each finger. These structures are then wire bonded for electrical characterisation as supercapacitors [10]. It is also a way

for checking that the interdigitated electrodes are not short-circuited by the activated carbon.

## 5. Conclusion

The ink jet deposition technology features unique capabilities in terms of materials deposition that cannot be achieved in any other way; the activated carbon example given in this paper demonstrates that good results can only be obtained if the ink jet deposition and the substrate surface condition are fully controlled. This method allows depositions smaller than the nozzle diameter to be achieved, resulting in a higher resolution for a technology which is limited by the inkjet head fabrication constraints or which requires parameter control conditions for the jets [11] which are difficult to master and impossible to implement on certain machines. The developed process consisting in surface functionalizing and suspension improvement through surfactant can be extended to other types of materials in suspension such as nanoparticles. This technique could be adapted for batch processing use of multihead could assure a high throughput.

## 6. Acknowledgement

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