Short communication

Elaboration of a microstructured inkjet-printed carbon electrochemical capacitor

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ABSTRACT

Carbon-based micro-supercapacitors dedicated to energy storage in self-powered modules were fabricated with inkjet printing technology on silicon substrate. An ink was first prepared by mixing an activated carbon powder with a PTFE polymer binder in ethylene glycol stabilized with a surfactant then deposited by inkjet on patterned gold current collectors with the substrate heated at $140\,°C$ in order to assure a good homogeneity.

Electrochemical micro-capacitors with electrodes in an interdigital configuration were fabricated, and characterized using electrochemical techniques in $1\,M$ Et_4NBF_4 propylene carbonate electrolyte. These micro-devices show an excellent capacitive behavior over a wide potential range of $2.5\,V$ for a cell capacitance of $2.1\,mF\,cm^{-2}$. The newly developed technology will allow the integration of the storage device as close as possible to the MEMS-based energy harvesting device, minimizing power losses through connections.

1. Introduction

The development of autonomous electronic miniaturized devices has lead to an increasing demand for rechargeable micro-power sources of appropriate size. Li and Li-ion micro-batteries have been developed for this purpose in the late 1990s [1,2]. On the other hand, harvesting micro-devices extracting energy from various ambient environment sources (thermal, mechanical, solar energy) have started to be developed in the year 2000 leading to self-powered systems [3–5]. The harvested energy may be stored in micro-batteries [6,7], but their finite life-time may be a major problem when they have to be embedded in permanent structures, such as biomedical implants [8], active Radio Frequency Identification (RFID) tags [9] and structure-embedded micro-sensors where no maintenance or replacement is possible [10]. Moreover, the quite low power densities of rechargeable batteries remain insufficient for some specific applications or power harvesting devices.

Electrochemical capacitors (ECs), also called supercapacitors, store energy using accumulation of ions at the interface between a highly porous electrode and an electrolyte. The charge storage mechanism is mainly capacitive, with no chemical modification of the electrode involved during the charge/discharge process. As a result, they can sustain millions of cycles, can provide fast charge/discharge rates and subsequently high power density, while keeping a reasonable energy density [11,12]. EC miniaturized to a microscopic scale could satisfy in this sense a variety of micro-power demands and complement or replace micro-batteries in electrical energy storage and harvesting applications where high power delivery or uptake pulses are required in very short times.

Very little work has been published on the integration of low-profile supercapacitors on a chip, although the applications are there: local power sources for Micro-Electro-Mechanical Systems (MEMSs) devices, intermediate storage level for energy harvesting microsystems and numerous sensors.

Micro-supercapacitors based on pseudocapacitive materials have been reported in literature with interdigital fingers as low as $50\,\mu m$ [13,14]. Unfortunately, the operating voltage range of these devices using hydrogel-polymer electrolyte hardly exceeds $1\,V$ [15], making them non-functional for most applications.

Yoon et al. have investigated the use of a pseudocapacitive amorphous RuO_2 electrode with a LiPON solid electrolyte for the elaboration of a thin-film micro-supercapacitor [16,17]. Despite the use of Li^+ ions instead of protons H^+ intercalation in RuO_2 electrode, they obtained a good capacitance and a high potential window.

Unlike pseudocapacitive materials, carbon-based active materials exhibit true capacitive behavior and excellent chemical stability upon cycling [18]. Ho et al. have developed a $5\,mm \times 5\,mm$ carbon EC using a direct write pneumatic dispenser printer

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[19]. They obtained a cell capacitance of $0.1\,mF\,cm^{-2}$ for a 2 V potential range, despite the use of carbon of low surface area.

The first microstructured carbon-based EC was reported by In et al. with an electrode area of $350\,\mu m \times 350\,\mu m$ using the Origami™ process [20]. Their micro-EC displays a cell capacitance of $0.4\,mF\,cm^{-2}$ for a 0.6 V potential range using aqueous electrolyte.

The use of hydrogel-polymer electrolyte for the elaboration of all solid-state thin-film carbon-based EC has also been reported by Kaempgen et al. with an estimated cell capacitance of $1.1\,mF\,cm^{-2}$, but a potential window limited to 1 V [21].

In the present work, a new process based on the inkjet printing technology is presented to integrate a microstructured carbon-based EC of high surface area on silicon with very few technological steps. The inkjet deposition technology has been developed for polymers [22], oxides [23], metals [24] and nanoparticles, and turns out to be interesting in various applications, but so far, no study of the deposition of activated carbon has been reported by this technique. Various micro-supercapacitors were designed with this technique with interdigital fingers ranging from 40 to $100\,\mu m$ width. The developments necessary for the inkjet deposition of the active material are described in the first part. Then, the electrochemical characterizations of the realized micro-supercapacitors are presented and the results discussed. These devices display excellent stabilities and electrochemical behaviors over a wide potential window.

2. Experimental

Micro-supercapacitors were designed as shown in Fig. 1. Two gold current collectors made of 20 interdigital fingers were deposited by evaporation on an oxidized silicon substrate, and patterned using a conventional photolithography/etching process. Activated carbon electrodes were deposited by a process based on the inkjet printing technology using
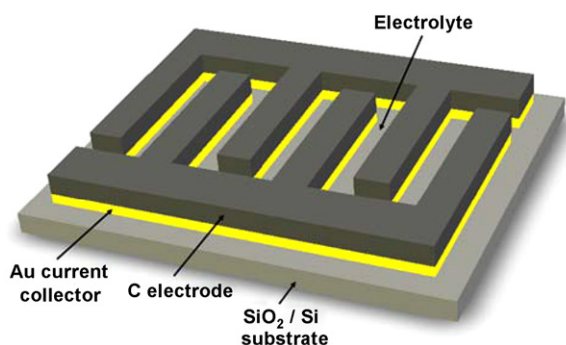

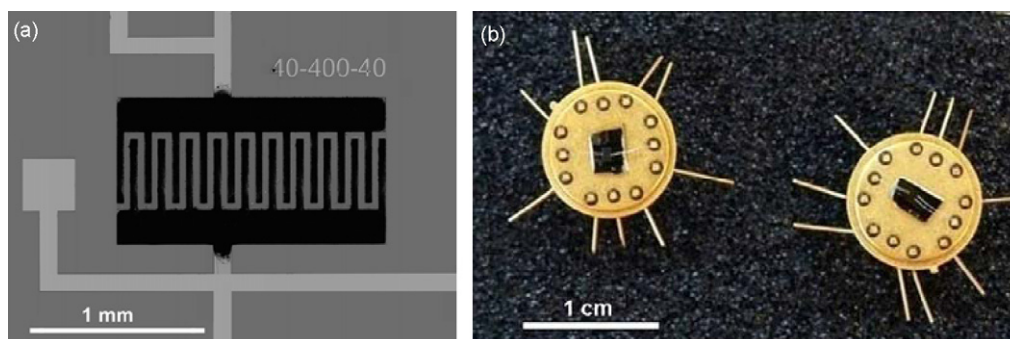**Fig. 1.** Schematic drawing of the interdigital micro-supercapacitor.

an AltaDrop® equipment from Altatech and detailed hereafter.

2.1. Process developments

Silicon dioxide (150 nm) was first grown on silicon wafer by plasma enhanced chemical vapour deposition (PECVD) followed by the evaporation of 150 Å of titanium and 300 nm of gold. The electrodes patterns on which activated carbon had to be fixed were formed by photolithography and etching of the titanium/gold layer.

A stable ink was then prepared by mixing an activated carbon of high surface area (1700–$1800\,m^2\,g^{-1}$ for a $92\,F\,g^{-1}$ electrode capacitance, Kuraray Chemical Co.) with 5 wt.% polytetrafluoroethylene (PTFE) polymer binder in an ethylene glycol solvent. The activated carbon composition was set to 3% weight relative to ethylene glycol. A Triton X100 (p-(1,3,3,-tetramethylbutyl) phenoxy-poly(ethylene glycol)) surfactant was added to the solution in order to increase the wettability and the stability of the emulsion [25].

This ink was then selectively projected onto the interdigital gold fingers. For this purpose, a hydrophobic surface functionalisation of the silicon dioxide was performed by means of an octadecyltrichlorosilane (OTS) treatment. The gold was therefore more hydrophilic, i.e. with a higher surface energy, than the surrounding hydrophobic silica surface, allowing thus the deposition of the ink onto the gold electrodes acting as current collectors.

The substrate temperature was fixed at 140 °C during the inkjet deposition in order to have an instantaneous evaporation of the droplets during impacts and get a homogeneous activated carbon deposition located exclusively on the metal patterns. The electrodes were finally annealed at a temperature of 240 °C.

2.2. Electrochemical characterizations

The two-electrodes EC micro-devices were characterized with a 1 M Et_4NBF_4/anhydrous propylene carbonate electrolyte in a glove box under Ar atmosphere with H_2O and O_2 levels less than 1 ppm (in order to prevent any early oxidation of the electrolyte), using a Biologic VMP potentiostat. Electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential by applying a sinusoidal signal of 10 mV amplitude and frequencies ranging from 100 kHz to 10 mHz.

3. Results and discussions

3.1. Design of the micro-device

Fig. 2(a) shows the image of a micro-supercapacitor with the following dimensions: 20 fingers, $40\,\mu m$ wide (w), $400\,\mu m$ long (L)

Fig. 2. Optical image of (a) a micro-supercapacitor with 20 fingers, $40\,\mu m$ wide, $400\,\mu m$ long and interspaced by $40\,\mu m$ and (b) the chips at lower magnification.

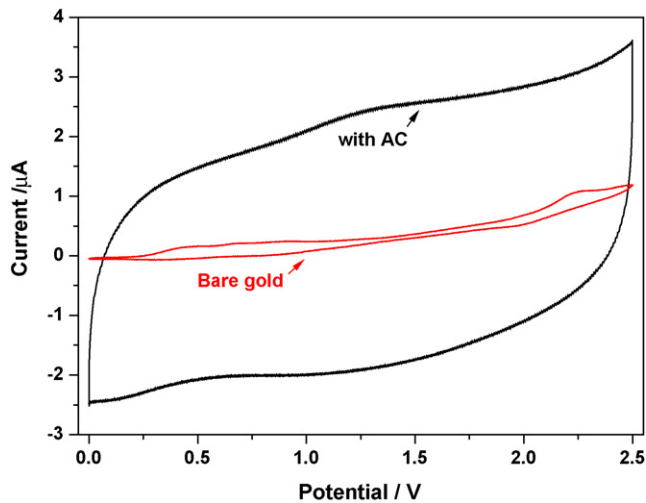**Fig. 3.** Cyclic voltammograms of a micro-supercapacitor uncoated and coated with activated carbon electrodes in 1 M Et_4NBF_4 propylene carbonate electrolyte at a scan rate of $100\,mV\,s^{-1}$.

Fig. 4. Evolution of the capacitive current (total cell surface $2.295\,mm^2$) deduced from CV carried out at different scan rates.

and 40 μm of interspace (i). Gold micro-wires were then bonded from the micro-device to the package for electrochemical characterization (Fig. 2(b)).

A homogeneous deposition of activated carbon is observed on the micro-supercapacitor, with a well defined pattern and no short circuit between the interdigital electrodes. The thickness of the activated carbon deposit estimated from confocal microscopy varies between 1 and 2 μm depending on the micro-device sample.

3.2. Electrochemical characterizations

Fig. 3 shows the cyclic voltammogram (CV) performed on a 75 μm wide (w), 750 μm long (L) and 75 μm of interspace (i) assembled micro-supercapacitor at a scan rate of 100 mV s^{-1} in 1 M Et_4NBF_4 propylene carbonate. The total surface of the conducting electrodes is $2.295\,mm^2$ ($0.585\,mm^2$ pad and $0.5625\,mm^2$ fingers). It displays a symmetrical capacitive behavior with the typical rectangular shape as expected for double layer capacitive materials. The weak redox wave observed at about 1.3 V could be attributed to the redox reactions of electroactive surface functional groups present on the carbon [26] or could be due to a variation of the capacitance with the potential.
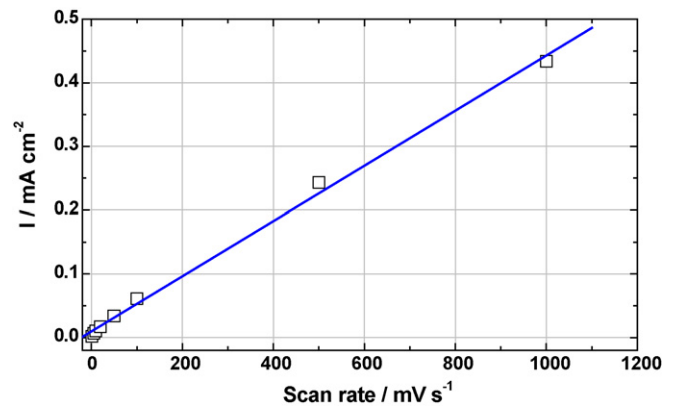
To verify the capacitance provided by the microstructured carbon electrodes, an identical micro-device with bare gold electrodes was tested in the same conditions (Fig. 3). We can clearly observe an important increase of the current during the CV, directly related to the capacitance and the energy of the carbon micro-supercapacitor.

Inkjet-printed micro-supercapacitors display moreover excellent capacitive behaviors over a wide potential range of 2.5 V in controlled atmosphere. This potential range allows the use of micro-supercapacitors in various mobile electronic applications, and could satisfy in this sense the growing need for integrated energy storage solutions.

Fig. 4 clearly shows a linear dependency of the capacitive current as a function of the scan rate. This current was calculated at discharge reversal scan and it was averaged over the whole voltage window. Since ion adsorption occurring upon charge processes in supercapacitor electrodes involves surface phenomena this kind of plot is typical for such electrochemical systems [27]. A small deviation would imply an under diffusion control process as it is the case, for example, at high rate for Faradaic reactions.

A mean cell capacitance of 0.4 mF cm^{-2} is deduced from the slope of Fig. 4, and a maximal cell capacitance $C_T = 2.1$ mF cm^{-2} is found at low scan rate (1 mV s^{-1}), which is the highest value reported for carbon EC micro-devices [19–21]. The estimated stack capacitance lies between 1.6 and 2.7 F cm^{-3} and the maximal energy density we can obtain for the micro-device for a 2.5 V potential range is 6.6 mJ cm^{-2}.
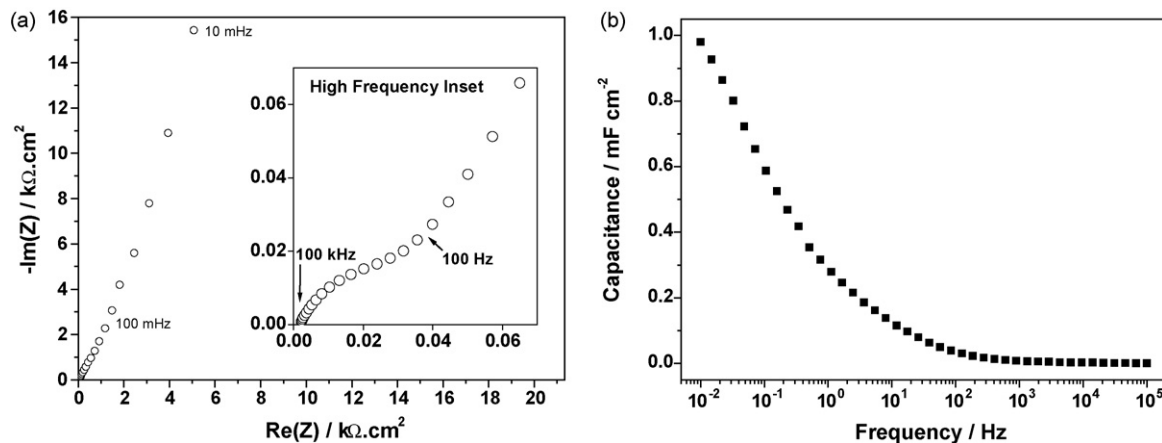

Fig. 5. (a) Nyquist plot of a micro-supercapacitor ($2.295\,mm^2$) and (b) evolution of the specific cell capacitance vs. the frequency.

3.3. Electrochemical impedance spectroscopy (EIS) measurements

The frequency behavior has been studied by EIS at a bias voltage of 0 V. Fig. 5(a) shows the Nyquist plot of a micro-supercapacitor, and Fig. 5(b) the evolution the specific capacitance as a function of the frequency, calculated from [28].

A micro-power of 44.9 mW cm^{-2} was estimated from the high frequency part of the spectrum. When the frequency is decreased from 100 Hz down to 10 mHz, the imaginary part of the impedance increases corresponding to a capacitive behavior of the micro-supercapacitor (Fig. 5(a)), associated with a leak resistance as can be seen from the slope with an angle lower than 90° [29].

The impedance frequency behavior was also studied using the frequency dependence of the complex capacitance (Fig. 5(b)). At 10 mHz, the specific capacitance is 1.0 mF cm^{-2}, which is consistent with the results obtained with CV (Fig. 4). The maximum capacitance is nevertheless obtained for frequencies lower than 10 mHz, revealing a high relaxation time constant τ_0 of the micro-device (and therefore a relative low power density), due probably to the slight leakage current. Microstructured inkjet-printed EC show therefore very promising electrochemical results. Future work will be performed on the chemical formulation of the initial ink and heat post-treatments of the devices in order to have micro-supercapacitors with higher electrochemical performances and lower leakage current.

4. Conclusions

An integration process for micro-supercapacitors was presented with a specific inkjet printing technology. Micro-supercapacitors with interdigital fingers as low as 40 μm width were obtained. Electrochemical characterizations in 1 M Et$_4$NBF$_4$ propylene carbonate reveal an excellent capacitive behavior of the micro-devices over a 2.5 V potential range, for a cell capacitance of 2.1 mF cm^{-2}. These results are very promising and demonstrate the viability of such technique for the elaboration of integrated micro-supercapacitors on Si substrate.

Future developments will consist in depositing thicker active material, optimizing the active material itself and providing a full device encapsulation. This technology of carbon-based micro-supercapacitors could address the need for micro-scale energy storage.

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