High resolution electrochemical micro-capacitors based on oxidized multi-walled carbon nanotubes

T M Dinh, D Pech*, M Brunet, A Achour
Laboratoire d’Analyse et d’Architecture des Systèmes, LAAS-CNRS
7 av du Colonel Roche, 31077 Toulouse Cedex 4, France.

*dpech@laas.fr

Abstract. This study reports the preparation of all-solid-state micro-supercapacitors in planar interdigitated configuration based on MWCNTs via the electrophoretic deposition technique. The carbon nanotubes were functionalized with carboxylic groups via a HNO₃ concentric solution in order to prevent their agglomeration and obtain a stable aqueous suspension, and to add a pseudo-capacitance contribution to the predominant double-layer capacitance. The electrode materials were characterized in a 3 electrode configuration, and the micro-devices in a two-electrode configuration using electrochemical impedance spectroscopy and cyclic voltammetry in 0.5 M sulfuric acid and a gel of PVA-H₃PO₄-H₂O doped by SiWA electrolyte. Spatial resolution down to 10 µm was obtained for the device with specific capacitance up to 1.8 mF.cm⁻² in electrolyte based PVA and a high power density of 1.28 W.cm⁻² in 0.5 M H₂SO₄ electrolyte.

1. Introduction
Electrochemical capacitors (also called supercapacitors) store electrical energy using the electrochemical double layer formed on electrode/electrolyte interface (electrochemical double layer capacitance EDLC) or the very fast and reversible electrochemical reaction on the surface of electrode (pseudo-capacitance) [1]. The miniaturization and the development of portable electronic devices such as wireless sensor networks and implantable medical devices, has led to an increasing demand for micro-power sources of appropriate size fulfilling specific requirements such as long lifetime, capability to charge and discharge at high rate and resistance to severe environments (low temperature in particular). On-chip micro-supercapacitors have shown therefore very interesting characteristics when it comes to these applications, because of their extended lifetime and high power density. In the last decade, the realizations of planar interdigitated micro-sized supercapacitors with resolution going from 500 µm to 5 µm were reported using the micro-fabrication process [2-13]. The best values of 10 and 5 µm have been obtained for our recent works with RuO₂ as active material using electrolytic deposition [12, 13]. One other way to obtain a high resolution for micro-supercapacitors is to use the selective electrophoretic deposition (EPD) of micrometric multi-walled carbon nanotubes (MWCNTs) particles onto patterned current collectors.

MWCNTs are well-known for their high specific surface area (can achieve 1315 m².g⁻¹ for one individual single-walled carbon nanotube [14]), a good electronic conductivity (3300-5000 S.cm⁻² [15]) which made them attractive electrode materials for powerMEMS devices [16]. The performance of supercapacitors based on MWCNTs is affected by physical properties of carbon electrodes as well
as the pore size distribution and the surface area. Apart from the physical structure, the chemical characteristics, such as the chemical stability, the contribution of heteroatoms on carbon surface can also influence the capacitor performance. In this work, oxygen-containing functional groups have been introduced onto the surface of carbon by concentric HNO$_3$ treatment to obtain a stable aqueous suspension, improve wettability, chemical reactivity and electrical properties. Then, the functional MWCNTs thin film has been produced onto gold current collector by EPD which has the advantages of short formation time, simple apparatus and suitability for mass production. The micro-supercapacitor built from EPD thin film electrodes and different electrolytes such as 0.5 M sulfuric acid and a gel proton conductor composing polyvinyl alcohol (PVA), phosphoric acid doped silicon tungstic acid (H$_2$SiW$_{12}$O$_{40}$, SiWA) in distilled water (PVA-H$_3$PO$_4$-SiWA-H$_2$O) offered a high power density and small equivalent series resistance (ESR) [17]. In addition, the gel polymer electrolyte is a potential candidate for encapsulation of the final device.

2. Experimental
Commercial MWCNTs (Nanostructured & Amorphous Materials, Inc., Houston, USA, > 95% purity) were oxidized in 15 mol.l$^{-1}$ HNO$_3$ stirring solution for 8h at 120°C. The powder was then successively washed with distilled water, rinsed with ethanol and dried at 80°C. The obtained powder was named O-MWCNTs. A stable suspension of 50 mg O-MWCNTs in 100 ml distilled water were prepared by ultrasonic dispersion for 1h. The zeta potential and size distribution of the suspension were measured using Zetasizer Nano ZS (Malvern Instruments, Ltd, UK). X-ray photoelectron spectroscopy (XPS) was used to determine the surface groups on the MWCNTs before and after acid treatment.

Micro-devices were prepared as follow. SiO$_2$ layer was first thermally oxidized on four inch silicon wafers to provide a good electrical insulation. Different interdigitated electrode series were then realized. 100 nm Ti and 400 nm Au were evaporated onto the substrate and patterned via a lift-off process. After that, the current collectors were protected by an insulating SU8 masking layer. To improve the resolution of the micro-device, a N-LOF photoresist was deposited in the gap between the electrodes. Afterwards, 50 nm of Au layer was deposited on the whole wafer, followed by the electrophoretic deposition of the active material. Both Au and O-MWCNTs layers on the unwanted areas were then lift-off to obtain the final devices.

The electrophoretic deposition was performed between a 2 cm$^2$ gold plate (negative electrode) and the positive target electrode of 0.25 cm$^2$ electrode and the micro-pattern before the second lift-off step. The DC voltage applied was 50 V and the distance between two electrodes was 0.5 cm. The EPD duration was set to 60s and 30s for 0.25 cm$^2$ electrodes and micro-device, respectively. The obtained deposit was annealing at 100°C for 1h to remove the remainder water.

The morphology and the thickness of O-MWCNTs thin films were observed using a field emission scanning electron microscopy Hitachi S-4800, Japan. The electrochemical behaviors of the O-MWCNTs electrodes as well as the micro-supercapacitors were analyzed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) on a potentiostat/galvanostat (SP 240 from BioLogic). All three-electrode configuration experiments were carried out using Ag/AgCl (KCl sat’d) and Pt wire as reference and counter electrodes, respectively. EIS measurements of the cell were made at chosen potential values with 10 mV amplitude and frequencies ranging from 100 kHz to 10 mHz.

3. Results and Discussion

3.1. Oxidation of CNTs
The preparation of the stable dispersion of MWCNTs in a suitable solvent is a necessary prerequisite for successful EPD. The MWCNTs treated in this way were negatively polarized that electrostatically stabilizes the aqueous suspension for long periods (zeta potential of -35.7 mV). The nanoparticle average size obtained is 65.7 nm that is in favour of the EPD process and the realization of supercapacitors with the high resolution.
The oxygen functional groups can be detected by XPS shown in figure 1. The C 1s spectrum is composed of C= C or C-H (~284.55 eV), C-O (285.90 eV), O=C-O (288.78 eV) functional groups. The results revealed that the MWCNTs have been successfully decorated by hydroxyl (-OH) and carboxyl (-COOH) groups during the concentric HNO₃ treatment at 120°C.

![Figure 1. C 1s spectrum for MWCNT and O-MWCNT deposits.](image)

3.2. Electrochemical characterizations of the electrodes.

The CV curve of O-MCNTs (figure 2a) displays a rectangular shape with good symmetry showing a typical electric double layer capacitive behaviour. The reversible peaks at 0.3 and 0.4 V vs. Ag/AgCl can be attributed to the pseudo-capacitive behaviour of the carboxyl-groups incorporated on the O-MWCNT structure as the results of the nitric acid treatment [18]. In an acid electrolyte, the hydrogen adsorption/desorption increases the apparent capacitance:

\[
\text{CNTs} - \text{COOH} + \text{H}^+ \leftrightarrow \text{CNTs} - \text{COOH}/\text{H}^+
\]

![Figure 2. Electrochemical characterizations of O-MWCNT deposits in deaerated 0.5 M H₂SO₄: a) CV curve of O-MWCNTs coated 0.25 cm² gold electrode at the scan rate of 500 mV.s⁻¹, b) Nyquist plots of O-MWCNT deposits at 0.3 and 0.4 V vs. Ag/AgCl and 0 V vs. open circuit voltage (OCV).](image)
The capacitance characteristics of the material were shown in figure 2b with the near straight lines in the low-frequency region which also revealed the absence of the leakage current. The straight line at 0 V vs. OCV where no electrochemical reaction occurs is typical of the double layer capacitance behaviour. This capacitance is lower than the pseudo-capacitance observed at 0.3 and 0.4 V vs. Ag/AgCl.

3.3. Realization of all-solid-state high resolution micro-supercapacitors.

Figure 3 shows the image of a micro-supercapacitor based on O-MCNTs after the second lift-off with the following dimensions: 100 µm wide, 900 µm long and 10 µm interspace. A homogeneous deposition of O-MWCNTs is observed on the micro-supercapacitor, with a well-defined patterned and no short circuit between the 10 µm interspaced electrodes. The electrophoretic bath does not damage the lift-off photoresist during the EPD process, and high resolution micro-EDLCs were therefore successfully realized. The electrochemical performances of the micro-device was characterized in a conventional deaerated 0.5 M H₂SO₄ aqueous electrolyte and using an all-solid state PVA-H₃PO₄-SiWA polymer electrolyte. The gel electrolyte was obtained by immobilizing the SiWA proton conductor in a polyvinyl alcohol matrix (PVA - H₃PO₄) [17].

![10 µm interspace O-MWCNT supercapacitor.](image)

The figure 4a presents the Nyquist plots of a 10 µm interspace micro-supercapacitor in these different electrolytes. When the frequencies decrease to 10 mHz, the imaginary part of the impedance increases according to the capacitive behavior of a capacitor. The ESR of the micro-device in sulfuric acid is smaller than polymer electrolyte that related to the ionic conductivity of these electrolytes [12]. These both small values of the ESR show the very high electronic conductivity of the electrode material. The CV curves of 10 µm interspace supercapacitor show a rectangular and symmetric shape for the capacitive behavior. For the same device, the polymer electrolyte provides a higher capacitance. This result can be explained by the oxidation/reduction of adsorbed SiWA electrolyte species next to the oxidation/reduction of –COOH groups [19]:

$$\text{SiW}_{12}\text{O}_{40}^{4-} + e + H^+ \leftrightarrow H\text{SiW}_{12}\text{O}_{40}^{4-}.$$
4. Conclusions

In this work, we have successfully developed an all-solid-state electrochemical micro-capacitor with 10 µm resolution. An energy density of 0.7 mJ.cm⁻² and a power density of 1.28 W.cm⁻² were obtained for the micro-cell with the PVA-H₃PO₄-SiWA electrolyte. The polymer electrolyte offered suitability for an encapsulation final device.

References

[1] Simon P and Gogotsi Y 2008 Nature materials 7 845-854
[2] Wang K, Zou W, Quan B, Yu A, Wu H, Jiang P and Wei Z 2011 Adv. Energy Mater.1 1068-1072
[3] Ajayan P M and Yakobson B I 2011 Nature Materials10(6) 415-417.
[4] Lin J, Zhang C, Yan Z, Zhu Y, Peng Z, Hauge R H, Natelson D and Tour J M 2013 Nano Lett.13 72-78
[5] Huang P, Heon M, Pech D, Brunet M, Taberna P L, Gogotsi Y, Lofland S, Hettinger J D and Simon P 2013 J. Power Sources225 240-244
[6] Pech D, Brunet M, Durou H, Huang P, Mochalin V, Gogotsi Y, Taberna P L and Simon P 2010 Nature Nanotech. 5651-654
[7] Durou H, Pech D, Colin D, Simon P, Taberna P L and Brunet M 2012 Microsyst. Technol.18 467-473
[8] Pech D, Brunet M, Taberna P L, Simon P, Fabre N, Mesnilgrente F, Conédéra V and Durou H 2010 J. Power Sources195 1266-1269
[9] Shen C, Wang X, Li S, Wang J, Zhang W and Kang F 2013 J. Power Sources234 302-309
[10] Chen C H, Tsai D S, Chung W H, Lee K Y, Chen Y M and Huang Y S 2012 J. Power Sources205 510-515
[11] Shen C, Wang X, Zhang W and Kang F 2011 J. Power Sources196 10465-10471
[12] Dinh T M, Armstrong K, Pech D, Brunet M, Gaudet J and Guay D 2013 Book of Abstract ISEECap (Taormina) p 84
[13] Pech D, Brunet M, Dinh T M, Armstrong K, Gaudet J and Guay D 2013 J. Power Sources230 230-235
[14] Peigney A, Laurent Ch, Flahaut E, Bacsa R R and Rousset A 2001 Carbon 39 507-514
[15] Ma R Z 1999 Materials Research Bulletin 34 741–747
[16] Inagaki M, Konno H and Tanaike O 2010 J. Power Sources 195 7880-7903
[17] Gao H, Ting Y J, Kherani N P and Lian K 2013 J. Power Sources 222 301-304
[18] Hu C G, Wang W L, Wang S X, Zhu W and Li Y 2003 Diamond and Related Materials 12 1295-1299
[19] Tian Q and Lian K 2010 Electrochemical and Solid-State Letters 13 A4-A6