



Elaboration of a Microstructured Inkjet-Printed Carbon Electrochemical Capacitor

David Pech, Magali Brunet, Pierre-Louis Taberna, Patrice Simon, Norbert Fabre, Fabien Mesnilgrente, Véronique Conédéra, Hugo Durou

► To cite this version:

David Pech, Magali Brunet, Pierre-Louis Taberna, Patrice Simon, Norbert Fabre, et al.. Elaboration of a Microstructured Inkjet-Printed Carbon Electrochemical Capacitor. *Journal of Power Sources*, 2010, 195 (4), pp.1266-1269. 10.1016/j.jpowsour.2009.08.085 . hal-01443055

HAL Id: hal-01443055

<https://hal.science/hal-01443055>

Submitted on 27 Jan 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Elsevier Editorial System(tm) for Journal of Power Sources
Manuscript Draft

Manuscript Number:

Title: Elaboration of a Microstructured Inkjet-Printed Carbon Electrochemical Capacitor.

Article Type: Full Length Article

Keywords: Supercapacitors; Microdevices; Inkjet

Corresponding Author: Dr Magali Brunet,

Corresponding Author's Institution: LAAS-CNRS

First Author: David Pech

Order of Authors: David Pech; Magali Brunet; Pierre-Louis Taberna; Patrice Simon; Norbert Fabre; Fabien Mesnilgrete; Véronique Conédéra; Hugo Durou

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 interdigitated configuration (40 µm wide (w), 400 µm long (L) and 40 µm interspace (i)) were fabricated, and characterized using electrochemical techniques in 1 M Et₄NBF₄ propylene carbonate electrolyte. These micro-devices show an excellent capacitive behavior over a wide potential range of 2.5 V for a specific capacitance per electrode of 5.1 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.



CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE



Dr. Magali Brunet
Research Scientist at LAAS-CNRS
Laboratoire d'Analyse et d'Architecture des Systèmes

Pr. Bruno Scrosati
European Editor of Journal of Power Sources
Universita di Roma La Sapienza
Piazzale Adlo Moro 3
Roma, ITALIA

Toulouse, 16th April 2009,

Dear Pr. Scrosati,

Please find enclosed a paper entitled **'Elaboration of a Microstructured Inkjet-Printed Carbon Electrochemical Capacitor'** by D. Pech et al. that we wish to have published as an article in Journal of Power Sources.

This article reports the first results of a fabricated micro-sized carbon electrochemical capacitor on silicon substrate with promising performance. A specific technology with ink-jet printing was developed to deposit activated carbon with a high resolution.

I greatly hope that such an article, which is at the frontier between electrochemistry and microtechnologies will meet the journal high standards.

With my best regards,

Magali Brunet

Elaboration of a Microstructured Inkjet-Printed Carbon Electrochemical Capacitor.

David Pech¹, Magali Brunet^{1,*}, Pierre-Louis Taberna², Patrice Simon²,
Norbert Fabre¹, Fabien Mesnilgrente¹, Véronique Conédéra¹, Hugo Durou¹.

¹ Université de Toulouse, LAAS-CNRS, 7 av. du Colonel Roche, F-31077 Toulouse, France.

² Université de Toulouse, CIRIMAT-CNRS, 118 route de Narbonne, F-31062 Toulouse, France.

Keywords: Micro-Supercapacitors; Microdevices; Inkjet;

* To whom correspondence should be addressed. Email: mbrunet@laas.fr

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 interdigitated configuration (40 μm wide (w), 400 μm long (L) and 40 μm interspace (i)) 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 specific capacitance per electrode of 5.1 $\text{mF}\cdot\text{cm}^{-2}$. 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] and [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] and [4]. The harvested energy may be stored in micro-batteries [5], but their finite life-time may be a major problem when they have to be embedded in permanent structures [6]. Moreover, the quite low power densities of rechargeable batteries remain insufficient for some specific applications or power harvesting devices.

Electrochemical capacitors (EC), 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 [7] and [8]. 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 (MEMS) 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 μm [9] and [10]. Unfortunately, the operating voltage range of these devices hardly exceeds 0.5 V, making them non-functional for most applications.

Unlike pseudocapacitive materials, carbon based active materials exhibit true capacitive behavior and excellent chemical stability upon cycling [11]. Ho *et al.* have developed a 5 x 5 mm² carbon EC using a direct write pneumatic dispenser printer [12]. They obtained a capacitance of 0.5 mF.cm⁻² per electrode for a 2 V potential range, despite the presence of water in their device.

In *et al.* have reported the first microstructured carbon-based EC with an electrode area of 350 x 350 μm^2 using the OrigamiTM process [13]. Their micro-EC displays a capacitance of 1.6 mF.cm⁻² per electrode for a 0.6 V potential range.

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 [14], oxides [15], metals [16] 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 μm width. These devices display an excellent stability and electrochemical behavior over a wide potential window of 2.5 V for a measured capacitance of 5.1 mF.cm⁻² per electrode.

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 ink-jet printing technology using 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 m².g⁻¹, 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 [17].

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 ink-jet 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-electrode EC microdevices were characterized with a 1 M Et₄NBF₄ / anhydrous propylene carbonate electrolyte in a glove box under Ar atmosphere with H₂O and O₂ 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 microdevice

Fig. 2. shows the image of a micro-supercapacitor with the following dimensions: 20 fingers, 40 μm wide (*w*), 400 μm long (*L*) and 40 μm of interspace (*i*), for a total surface of 0.64 mm² per electrode. Gold micro-wires were bonded from the micro-device to the package for electrochemical characterization.

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 microdevice sample.

3.2. Electrochemical characterizations

Fig. 3. shows the cyclic voltammogram (CV) of an assembled micro-supercapacitor at a scan rate of 100 mV.s⁻¹ in 1 M Et₄NBF₄ propylene carbonate. It displays an excellent

symmetrical capacitive behavior with the typical rectangular shape as expected for double layer capacitive materials, but it has to be emphasized that such CV has only been observed up to now for macroscopic supercapacitors.

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 [18] 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.

The figure 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 [19]. A small deviation would imply an under diffusion control process as it is the case, for example, at high rate for faradaic reactions.

A maximal capacitance value of $C_T = 5.1 \text{ mF.cm}^{-2}$ per electrode is found and a mean capacitance per electrode of 1.1 mF.cm^{-2} . The corresponding maximal energy density of the micro-device for a 2.5 V potential range is 15.9 mJ.cm^{-2} per electrode.

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 [20].

When the frequency is decreased from 10 kHz 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° [21].

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 1.2 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 $40 \text{ }\mu\text{m}$ width were obtained. Electrochemical characterizations in 1 M Et_4NBF_4 propylene carbonate reveal an excellent capacitive behavior of the micro-devices over a 2.5 V potential range, for a specific capacitance of 5.1 mF.cm^{-2} per electrode. 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.

Acknowledgements

This work was financially supported by the FRAE (Fondation de Recherche pour l'Aéronautique et l'Espace).

References

- [1] S.D. Jones and J.R. Akridge, *Solid State Ionics* **86-88** (1996) 1291-1294.
- [2] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda and C.D. Evans, *Solid State Ionics* **135** (2000) 33-45.
- [3] P.H. Humble, J.N. Harb and R. Lafollette, *J. Electrochem. Soc.* **148** (2001) 1357-1361.
- [4] S.P. Beeby, M.J. Tudor and N.M. White, *Meas. Sci. Technol.* **17** (2006) 175-195.
- [5] H.A. Sodano, G.E. Simmers, R. Dereux and D.J. Inman, *J. Intel. Mat. Syst. Str.* **18** (2007) 3-10.
- [6] J.Y. Kang, Micropower for Medical Application, in: J.G. Webster (Ed), *Encyclopedia of Medical Devices and Instrumentation*, Wiley, 2006.
- [7] J. R. Miller and P. Simon, *Science* **321** (2008) 651-652.
- [8] P. Simon and Y. Gogotsi, *Nat. Mater.* **7** (2008) 845-854.
- [9] J.-H. Sung, S.-J. Kim, S.-H. Jeong, E.-H. Kim and K.-H. Lee, *J. Power Sources* **162** (2006) 1467-1470.
- [0] W. Sun and X. Chen, *Microelectron. Eng.* (2009) In Press.

- [1] A.G. Pandolfo and A.F. Hollenkamp, *J. Power Sources* **157** (2006) 11-27.
- [2] C.C. Ho, D.A. Steingart, J.P. Salminen, W.H. Sin, T.M.K. Rantala, J.W. Evans and P.K. Wright, 6th Workshop on Micro and Nanotechnology for Power Generation and Energy Conversion, Berkeley, CA, November 29 - December 1, 2006.
- [3] H.J. In, S. Kumar, Y. Shao-Horn and G. Barbastathis, *Appl. Phys. Lett.* **88** (2006) 083104.
- [4] A. Morrin, O. Ngamna, E. O'Malley, N. Kent, S.E. Moulton, G.G Wallace, M.RM Smyth and A.J. Killard, *Electrochim. Acta* **53** (2008) 5092-5099.
- [5] T. Kaydanova, A. Miedaner, J.D. Perkins, C. Curtis, J.L. Alleman and D.S. Ginley, *Thin Solid Films* **515** (2007) 3820-3824.
- [6] L. Yang, A. Rida, R. Vyas and M.M. Tentzeris, *IEEE T. Microw. Theory* **55** (2007) 2894-2901.
- [17] V. Conédéra, F. Mesnilgrete, M. Brunet and N. Fabre, *Proceedings of ICQNM conference*, Cancun, Mexico, 1-7 February 2009.
- [8] M. Toupin, D. Bélanger, I.R. Hill and D. Quinn, *J. Power Sources* **140** (2005) 203-210.
- [19] P. Soudan, J. Gaudet, D. Guay, D. Bélanger and R. Schulz, *Chem. Mater.* **14** (2002) 1210-1215.
- [20] P.L. Taberna, P. Simon and J.F. Fauvarque, *J. Electrochem. Soc.* **150** (2003) 292.
- [21] B.E. Conway, W.G. Pell and T.-C. Liu, *J. Power Sources* **65** (1997) 53.

Figures Caption

Figure 1. Schematic drawing of the interdigital micro-supercapacitor.

Figure 2. Optical image of (a) the chips and (b) a 40 μm - 400 μm - 40 μm micro-supercapacitor.

Figure 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} .

Figure 4. Evolution of the capacitive current per electrode deduced from CV carried out at different scan rates.

Figure 5. (a) Nyquist plot of a micro-supercapacitor brought to the surface of one electrode – (b) Evolution of the specific capacitance per electrode vs. the frequency.

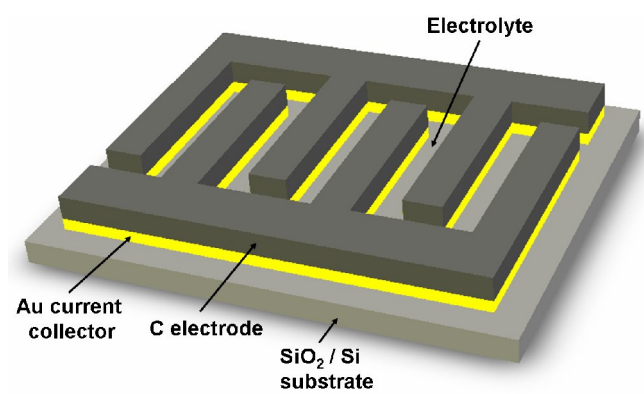


Fig. 1. Schematic drawing of the interdigital micro-supercapacitor.

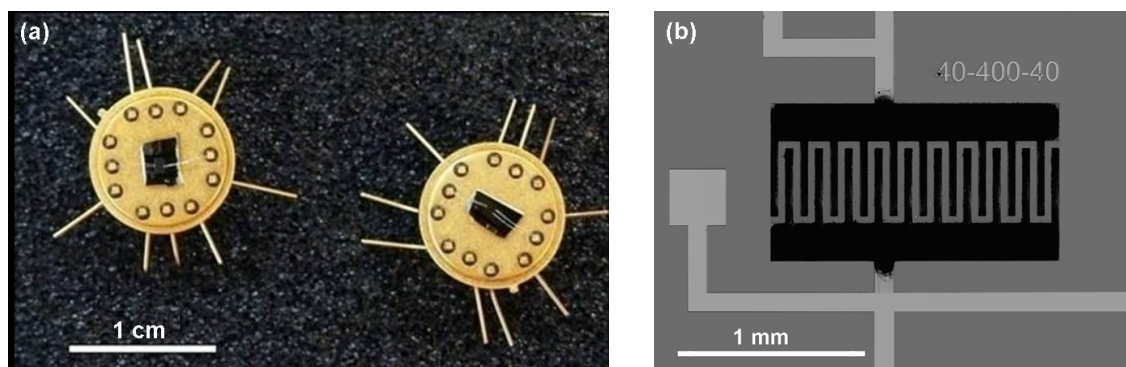


Fig. 2. Optical image of (a) the chips and (b) a 40 μm - 400 μm - 40 μm micro-supercapacitor.

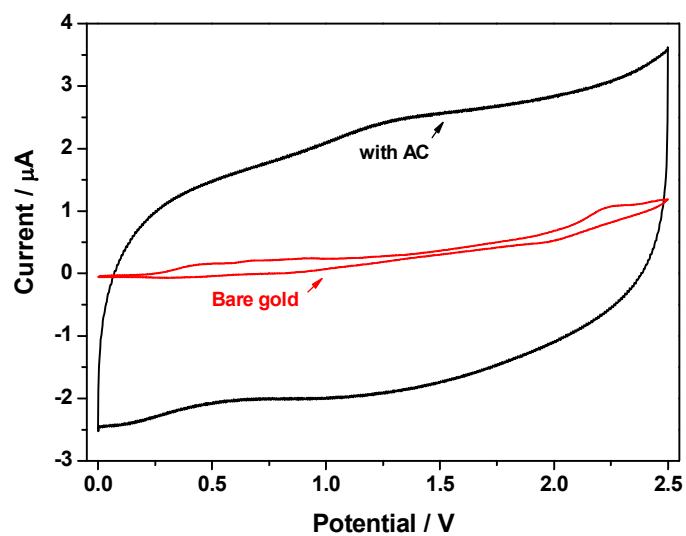


Fig. 3. Cyclic voltammograms of a micro-supercapacitor uncoated and coated with activated carbon electrodes in 1 M Et_4NBF_4 propylene carbonate electrolyte at a scan rate of 100 mV.s^{-1} .

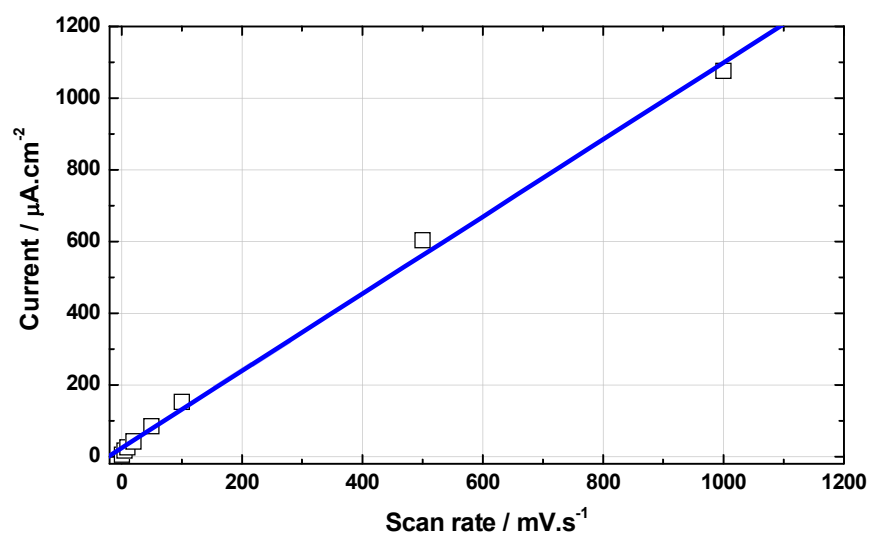


Fig. 4. Evolution of the capacitive current per electrode deduced from CV carried out at different scan rates.

Figure 5
[Click here to download Figure\(s\): Fig 5.doc](#)

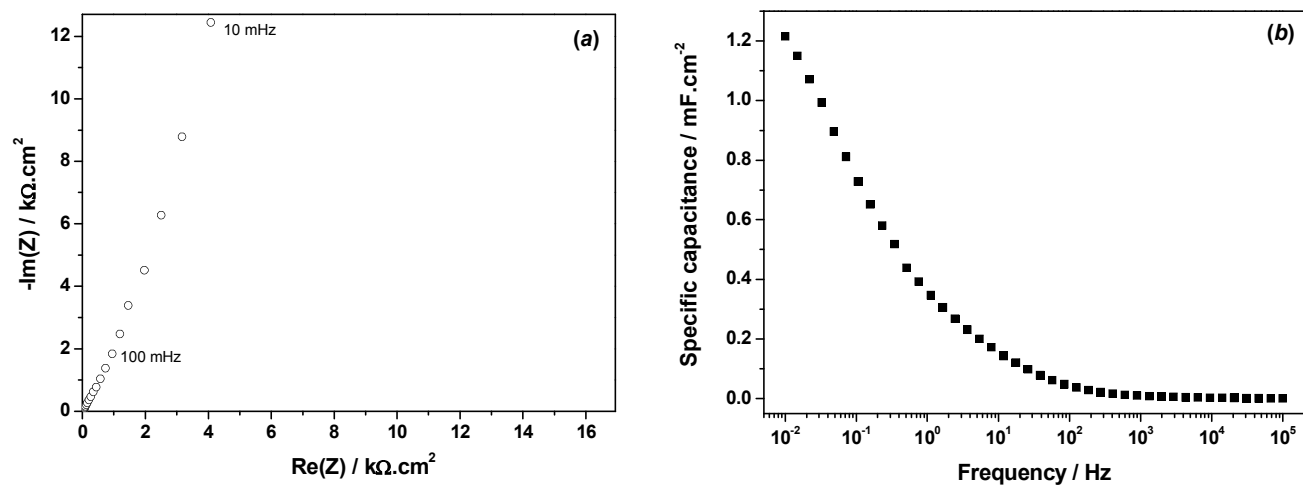


Fig. 5. (a) Nyquist plot of a micro-supercapacitor brought to the surface of one electrode –
(b) Evolution of the specific capacitance per electrode *vs.* the frequency.