Impact of the surface roughness on the electrical capacitance

A. Albina [a], P.L. Taberna [b], J.P. Cambronne [a], P. Simon [b], E. Flahaut [b] and T. Lebey [a]

[a] Electrical Engineering Laboratory, UMR 5003 UPS-CNRS, 118Route de Narbonne, 31062 Toulouse Cedex, France
[b] CIRIMAT, UMR CNRS 5085, 118 Route de Narbonne, 31062 Toulouse Cedex, France

Abstract

A new hybrid approach consists to use the advantages of both systems namely the high geometric aspects of the electrodes of the ultracapacitor and the high dielectric strength of polymer materials used in dielectric capacitors. The surface roughness of the electrodes of the ultracapacitor is manufactured with nano-porous materials; activated carbon and carbon nanotubes (CNTs).
Many compositions of both carbonaceous materials are tested with different insulating materials (liquid and solid) to constitute the hybrid capacitor. It appears that the capacitance increases with the carbonaceous composition: An increasing from 15 to 40% is observed as compared to a plane capacitor, it can be twice with a 100 wt% of CNTs content. But, the impregnation of the insulating material in the surface roughness remains the key point of the realization of the hybrid capacitor. The roughness accessibility is a major property to optimize in order to improve the impregnation of the insulating material to increase the electrical capacitance.

1. Introduction
2. Simulation: surface roughness effect on capacitance
3. Experimental
3.1. Synthesis of CNTs
3.2. Contribution of CNTs to the surface roughness of active layer
4. Realization of first hybrid capacitors
4.1. Hybrid capacitor with two rough electrodes
4.2. Hybrid capacitor with one rough electrode and one smooth electrode
4.3. Electrodes/dielectric material interfaces
5. Conclusion
References

1. Introduction

Integration of passive components is a major challenge and focuses an increasing interest in the packaging community today. Miniaturization of electronic components has an impact on the development of passive components, since their physical parameters must be taken into account more accurately to enhance electrical properties. Surface roughness is one of these parameters. Since the local conditions on the electric field are unknown, the classical analytic formulations of the capacitance cannot be applied anymore. Many works have already been devoted to this topic [1], [2], [3] and [4]. Hence, the impacts of surface roughness on electrical properties of a thin insulating film capacitor with one smooth electrode and one rough electrode were investigated in these papers and it was shown that capacitance increases with the surface roughness [1], [2] and [3].

In this paper, we present a new hybrid system. It is derived from the techniques used to assemble ultracapacitors electrodes (where mainly activated carbon and carbon nanotubes (CNTs) are employed) and using insulating material. These porous conductive materials offer specific surface areas from 500 to 2000 m^2/g. Carbon grain mean size is around 10 μm. They can be suitable to design surface microscopic roughness. Adsorbent properties of activated carbon-based ultracapacitors are known since antiquities and are largely used in many applications of purification.

Carbon nanotubes are carbonaceous materials with particular properties: high accessible surface area, low mass density and high electronic conductivity. In this paper, carbon nanotubes used are double-walled carbon nanotubes (DWNTs) [6]. DWNTs are particular Multi-Wall CNTs (MWCNTs) since they have the smaller number of concentric walls. For this reason DWNTs are expected to exhibit an intermediate behavior between SWNTs and MWNTs with number of walls higher than two.

In order to evaluate the change of the capacitance values versus surface roughness (or specific surface), a simulation is proposed in Section 1, using finite elements method.

In Section 2, surface roughness of electrodes obtained with conductive porous nanosystems is presented. Experimental details regarding the synthesis of CNTs and their contribution to the surface roughness as compared to the active layer based on activated carbon are given.

In Section 3, conclusions of the simulation are put into practice with the hybrid conception: a first capacitor is assembled with two rough electrodes.

Finally, a hybrid capacitor presenting with one smooth electrode and one rough electrode is realized. Electrical results are presented and discussed regarding mainly the impact on capacitance of the electrode/dielectric interfaces.

2. Simulation: surface roughness effect on capacitance

In an homogeneous and uniform electric field, the capacitance value C (F) of a capacitor of electrodes' surface S (m^2) and of dielectric thickness e (m) is calculated according to (1), where ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}) and ε_r the relative dielectric permittivity:

(1)

$$C = \varepsilon_0 \varepsilon_r \frac{S}{e}$$

But, when the surface roughness increases, the local conditions on the electric field become unknown; the classical analytic formulation (1) of the capacitance does not stand anymore. Many works deal with the modelling of the surface roughness. For example, Patrikar [1]: used a rough profile modelled by the Mandelbrot–Weierstrass function.

It is however possible to calculate the capacitance values from the density of electrical energy using finite element method [5]. In our case, based on a simple but representative geometry (teeth of saws see Fig. 1) of rough and disordered surfaces, the capacitance values may be calculated from the distribution of density of electrical energy U_e (J m^{-3}) according to (2).
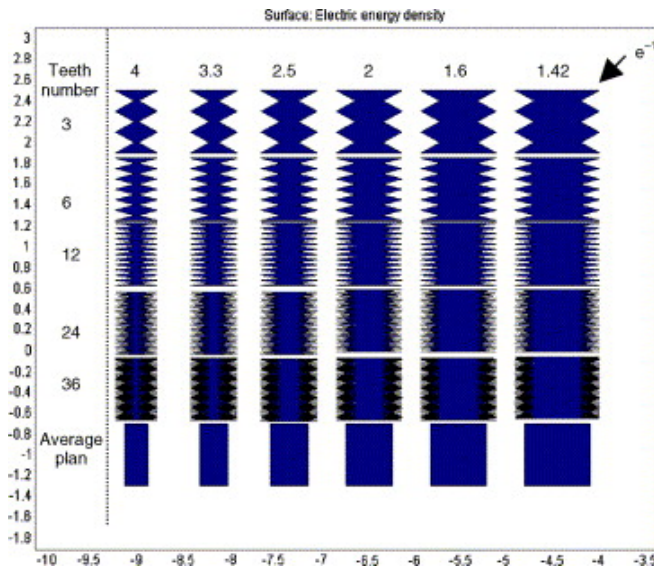
(2)

$$U_e = \frac{1}{2} C V^2$$

Fig. 1. Geometrical Figures proposed for the simulation. Electrodes are represented by outlines (Voltage V=10 V) and the dielectric material is represented by black areas (ε_r=3).

Different geometrical figures are proposed to make varied specific surface (Fig. 1). The surface roughness is characterised by the number of teeth per unit of length: the surface roughness then increases with the teeth number. The depth of teeth is identical in all geometrical figures, which allows defining an average plane of thickness 'e' located on the middle height of these teeth. The width of every plane represents the average dielectric thickness. Geometrical dimension are in arbitrary units: capacitance values are reported to these arbitrary units and the depth of teeth is 0.2.

The Fig. 2 shows that the capacitance values increase with the surface roughness and moreover that the lower the dielectric thickness is, the larger the capacitance increases; an exponential increase describes the evolution of the capacitance. This phenomenon is all the more marked when the thickness of dielectric is small. The capacitance tends to a limited value for large

surface area. The number of teeth increasing and the accessible surface for the electric field decreases. The field is being concentrated at the tip of the teeth.
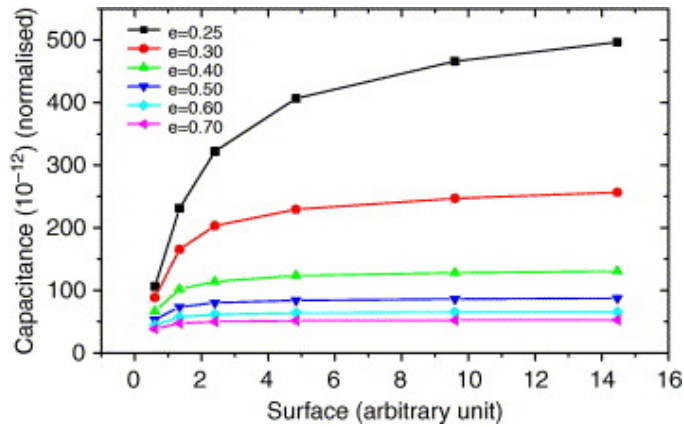

Fig. 2. Capacitance values (normalised) vs. surfaces for a given thickness.

Fig. 3 shows for a plane capacitor (surface=0.6, number of teeth=0), a linear change of capacitance values with the reciprocal of the dielectric thicknesses. It is interesting to note the non-linear behaviour of capacitance values with surface roughness for (surface=1.34, number of teeth=3) to (surface=14.47, number of teeth=36). These results demonstrate the impact of the surface roughness effect on the capacitance values in both a qualitative and a quantitative way.
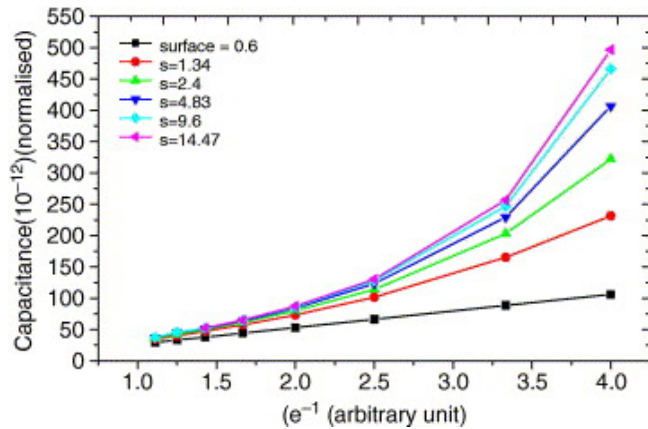

Fig. 3. Capacitance values (normalised) vs. reciprocal dielectric thicknesses.

In Fig. 4, the capacitance values are presented as a function of the ratio dielectric thickness/depth of teeth (0.2): the larger the ratio is, the higher the dielectric thickness is. Hence, in order to obtain high capacitance values using rough surface, it is necessary that the dielectric thickness is in the order of magnitude of the teeth size. In other words, in order to appreciate of the roughness, it is necessary to consider the distance between the electrodes.
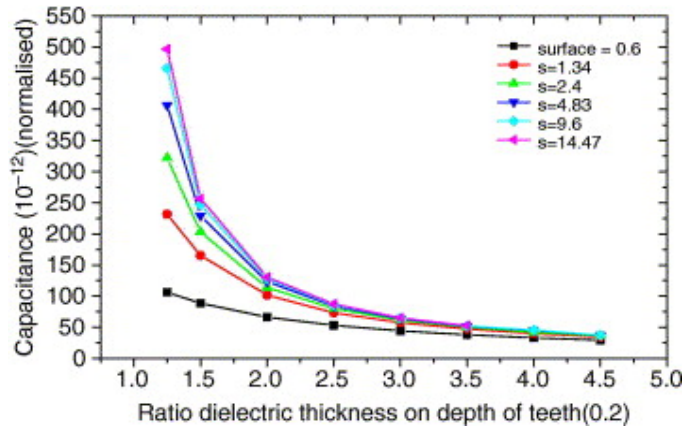
Fig. 4. Normalised capacitance values vs. the ratio of dielectric thickness on the depth of teeth (0.2).

All these results will be helpful during the dimensioning.

These simulation results are the starting point for experiments. Since the dielectric thickness has to be in the same order of magnitude that the roughness size, two parameters must be taken into account.

On the one hand, the surface roughness is related to the porous nano-materials (carbon nanotubes (CNTs) and activated carbon) (Fig. 5). The surface roughness size is around some micrometers. Therefore, the impregnation of the dielectric material by the surface roughness will not be trivial. An appropriate material in terms of viscosity at molten state and of its wettability must be carefully chosen. On the other hand, a rough and disordered surface generates a local reinforcement of the electric field; small thicknesses dielectric material could experience electrical breakdown: this is the reason why the dielectric material must therefore present a high dielectric strength.
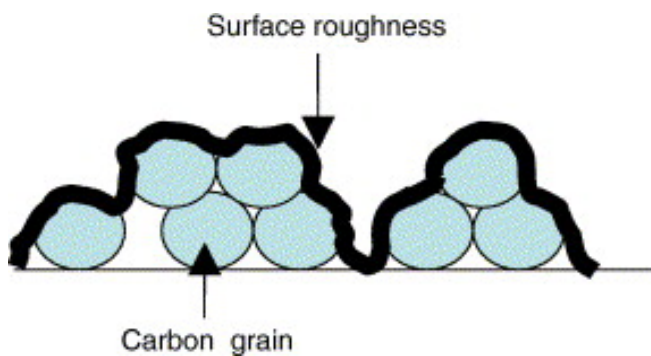

Fig. 5. Surface roughness of a carbonaceous thin film.

3. Experimental

3.1. Synthesis of CNTs

The CNTs are synthesised in gram-scale by catalytic chemical vapour deposition (CCVD) of a mixture of CH_4 (18% mol) in H_2 on a MgO-based catalyst, at a temperature of 1000 °C. The main interest of MgO-based catalysts is to be easily removable after the CCVD step, by dissolution in HCl. The catalyst, which can be written as $Mg_{0.95}(Co_{0.9}Mo_{0.1})_{0.05}O$, is not a solid solution (traces of an unidentified MoO_y oxide were detected by X-ray diffraction). Experimental details about the preparation of the catalyst have been reported elsewhere [6]. Each CCVD run produced around 3 g of CNTs. After the CCVD treatment, the so-obtained composite was reacted with concentrated aqueous HCl solution (37%) (Overnight at room temperature) in order to remove the catalyst. The product was then washed with deionised water on a filtration membrane, until neutrality was reached. CNTs (Fig. 6) are usually dried in air at 80 °C in order to obtain them in the form of a powder, but this leads to a strong agglomeration and makes their dispersion very difficult. In this work, the CNTs were not dried and were kept in deionised water to avoid agglomeration and thus facilitate the design of the active layer for electrodes.
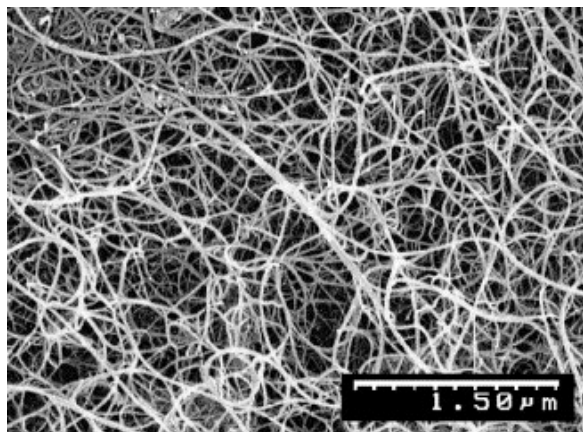

Fig. 6. MEB image of CNTs after catalyst reveals density of bundles of CNTs with extensive branching. They offer surface roughness from 500 to 600 m^2/g.

The CNTs are characterised by different techniques to control their purity. The carbon content was obtained by flash combustion and was found close to 80 wt%, which corresponds to 87.1 mol% assuming that the sample contains only cobalt and carbon. The BET surface area (the surface obtained corresponds to the accessible surface for adsorbed N_2 gas) is around 500–600 m^2/g. The remaining metal (12.9 mol%) is present in the sample as carbon-encapsulated nanoparticles. The metal is protected by the graphitic layers and thus is not subject to oxidation or to interaction with its environment. TEM observation of the CNTs and statistical analysis of the images of more than 180 individual CNTs revealed that the CNTs contain more than 70%

DWNTs (Fig. 7) and those tubes with up to six concentric layers were found (although in very small amount). The diameter distribution mainly ranges between 1 and 4.5 nm but a few tubes with a diameter lower than 1 nm were also observed.
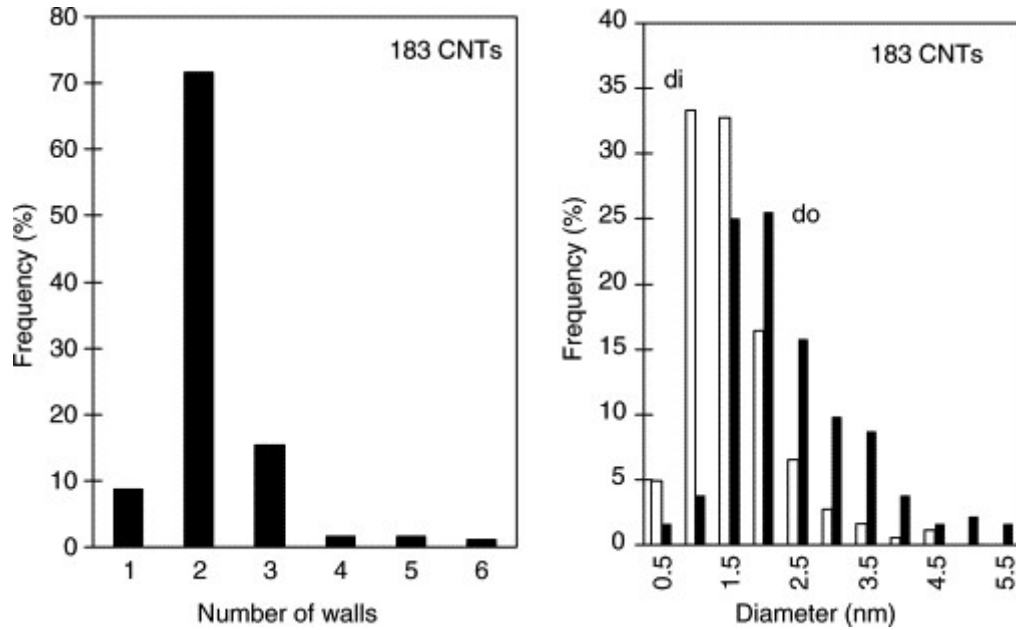

Fig. 7. Histograms showing the frequency distribution of the number of walls and diameters of the CNTs.

The sample was analysed by Raman spectroscopy (Fig. 8). The Raman, spectra gives two kinds of information about the sample: (i) between 100 and 300 cm^{-1}, the radial breathing modes (RBM) are strongly depending on the diameter of the CNTs and models have been proposed to calculate the diameter from the frequency of the RBM peaks [6], the CNTs have diameters ranging from 0.93 (peak no11 in the Fig. 8) to 2.41 nm (peak no1 in the same Fig. 8), assuming that the CNTs are gathered into small diameter bundles [6]; (ii) at higher frequency (between 1250 and 1700 cm^{-1}), the Raman spectra is characterised by two main bands centred at 1349.24 cm^{-1} (D peak corresponding to sp^3 carbon) and 1583.35 cm^{-1} (G peak corresponding to sp^2 carbon). The ration $I_{D/G}$ between the intensity of the D and the G bands is often used to quantify the degree of purity of the samples of CNTs, low values of $I_{D/G}$ corresponding to a better purity. The experimental value of $I_{D/G}$ is close to 8%, which corresponds to a good structural quality of the sample [6].
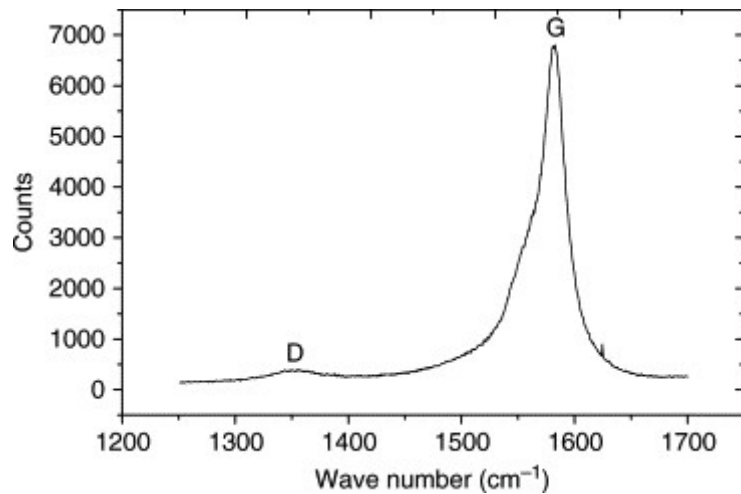
Fig. 8. Raman spectra of the CNTs. The ratio $I_{D/G}$ is around 8%. The D peak and the G peak correspond respectively to sp^3 and sp^2 carbon configuration.

3.2. Contribution of CNTs to the surface roughness of active layer

To constitute the active layer, activated carbon powders (PicactifBPIO from the PICA Company, Vierzon, France) (Fig. 9) and polytetrafluoroethylene (PTFE, from Dupont de Nemours) as binder are mixed together. The active layer composition is x wt% activated carbon, y wt% CNTs and 5% PTFE, with $x+y=95$. The content of CNTs in different active layer studied ranges between 0 and 100 wt%.
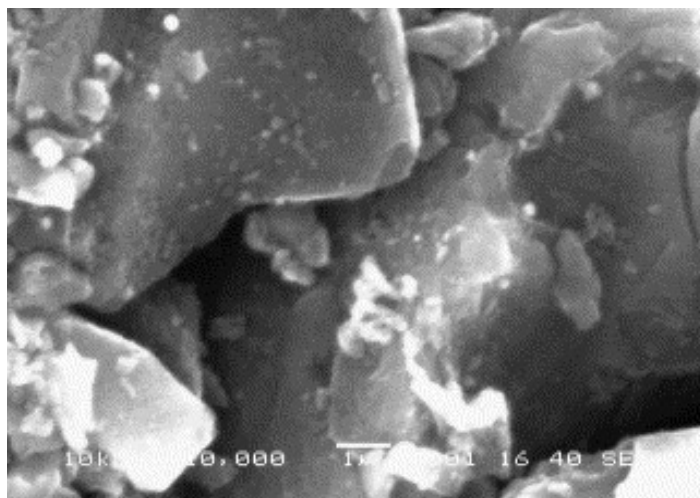

Fig. 9. SEM image of activated carbon (It corresponds to 0 wt% CNTs). The grain size is around 8 μm. They offer surface roughness from 1000 to 2000 m^2/g.

In the model and for the simulation, the impregnation of the dielectric material is maximal. In this case, the surface contact between the electrode and the dielectric material (or surface used by the dielectric material) is described by the whole surface roughness developed by the electrode. In real conditions, the impregnation of the dielectric material is more difficult and depends on a lot of parameters. When a polymer is used as dielectric material, it must have a weak viscosity at molten state. For a chemical vapour deposition of the dielectric, the deposition must be conformal to the surface roughness. As a conclusion and in opposition with the simulation, it is important to consider that the surface contact between an electrode and the dielectric material is not the whole surface roughness developed by the electrode. It is thus impossible to know the exact surface covered by the dielectric material when starting the experiments. Precisely, the following property will confirm this argument in the Section 3: the porous structure of electrodes constituted only with CNTs develops less surface area (500–600 m^2/g) than electrodes based on activated carbon (1000–2000 m^2/g). But the roughness accessibility is higher with CNTs (Fig. 10) than with the activated carbon (Fig. 9). The roughness accessibility offers a surface contact, which is more important, despite the decrease of the specific surface.
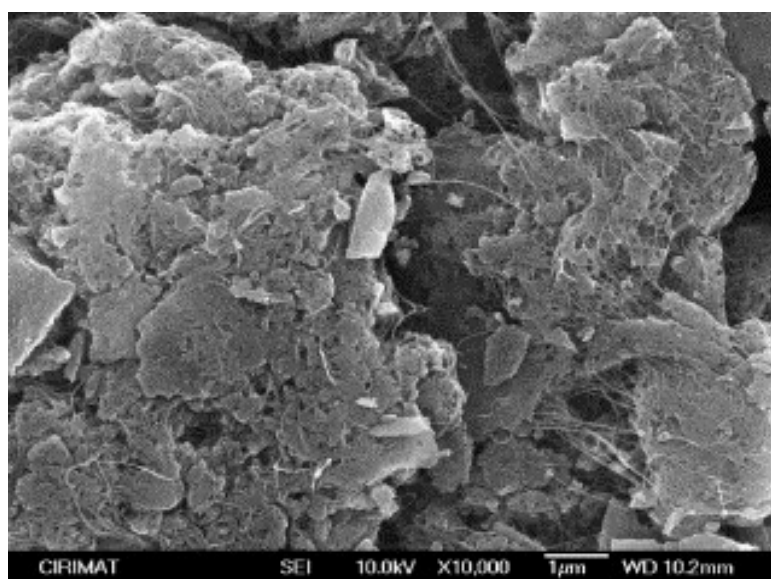

Fig. 10. SEM image of a sample of an active layer with 50 wt% CNTs.

4. Realization of first hybrid capacitors

To validate the conclusions of our simulation and the interest of using nanomaterials to design surface roughness, some hybrid capacitors were assembled.

4.1. Hybrid capacitor with two rough electrodes

These capacitors are constituted with two dielectric materials, a solid dielectric (thin film of kapton ε_r=3.2, thickness e=25 µm) and a liquid (silicon oil ε_r=2.9, viscosity=27 cP). The liquid dielectric fills open space left by the solid dielectric used as spacer between the two electrodes. The sample is kept under pressure during the electrical tests. Two types of composition of carbonaceous layers for the two electrodes are compared with the plane capacitor respectively one sample with 100% wt of activated carbon and one sample with 100% wt CNTs content. An impedance meter HP 4284 A is used to measure the capacitance versus frequency (from 20 Hz to 1 MHz) and voltage (from 1 to 10 V).
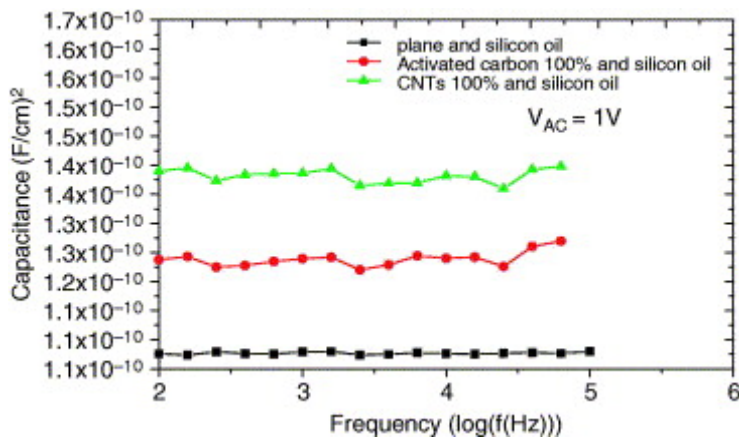Fig. 11 shows the change of capacitance values vs the frequencies at 1 V.

Fig. 11. Capacitance per unit area (F cm^{-2}) versus frequencies (log(f Hz)).

These electrical results are interesting. First, it can be seen that the capacitance values are not frequency dependent (at least in the frequency range under study).
Second, the impact of using carbonaceous layers as electrodes is obvious (as compared with plan capacitor). The accessibility to the surface is different between activated carbon and CNTs: the use of CNTs allows an increase of 30% as compared to planar electrodes whereas carbonaceous layer based on activated carbon only leads to an increase of 15%. The increase between the sample based on activated carbon and the sample based on CNTs around 12%. But, such an assembly using kapton film as spacer leads to a limitation for the oil impregnation, because of the mechanical pressure exerted on the sample. The accessibility of surface roughness for silicon oil is then limited. It is difficult to reach the whole roughness of porous nanosystems. These promising results show however the limitations of this system design.
Another type of hybrid capacitor has then been designed. In this configuration, one rough electrode and one smooth electrode are used without mechanical pressure [7]. Two compositions (50% wt CNTs and 100% wt CNTs) have been tested.

4.2. Hybrid capacitor with one rough electrode and one smooth electrode

A polyethylene film (PE) (relative permittivity ε_r=2.2) is used as dielectric material. The PE is placed on the surface of the active layer. The thickness of a thin film is 40 μm. Whatever the composition, the carbon layer/PE film electrode is then placed in a drying oven at 120 °C during 1 h without any mechanical pressure. During the viscoelastic phase, the swollen PE impregnates the surface roughness. After cooling the sample, a metallization using the sputtering of a gold target is achieved on the outer layer of PE. The second electrode of about 0.28 cm^2 is realized. The capacitance is measured versus the surface roughness at 1 KHz and for a voltage of 1 V. The surface roughness depending on the carbonaceous composition of active layer (Fig. 12).
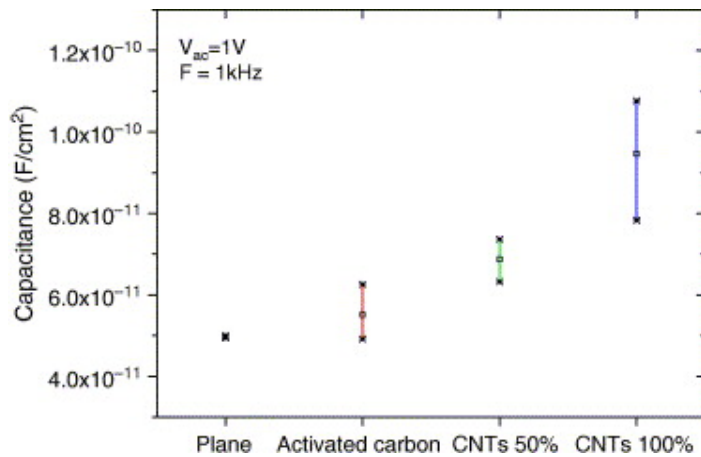

Fig. 12. Capacitance per unit area (F cm^{-2}) versus surface roughness (depending on active layer composition).

Significant changes are observed, the capacitance increases of 40% as compared to a plane capacitor. It can be twice by using a CNTs content of 100 wt%. But, for these high CNTs contents, the active layer is difficult to process and the mechanical strength is not homogeneous from a sample to another, leading to dispersion in the capacitance values measured. It will be necessary to improve the active film process.

These results show that there is a real difference between the experiments and the simulation results. As a matter of fact, the simulation result does not take into account an important parameter: the surface contact at the dielectric material/active layer interface is lower than the real surface of the electrode. Fig. 12 does not show that the capacitance increases with the surface roughness defined by the electrode, but that it is related to the surface accessible to the dielectric material. These are characteristics of the dielectric material in terms of thickness, viscosity and wettability.

4.3. Electrodes/dielectric material interfaces

Electrodes/dielectric material interfaces have been characterised by SEM. Fig. 13 presents a cross section of the interface PE—active layer with a tilt angle of 15°. The interface is located at the intersection of two arrows in dotted lines. The PE and the active layer adhering to the PE are located, respectively, on the left and on the right sides of this intersection.
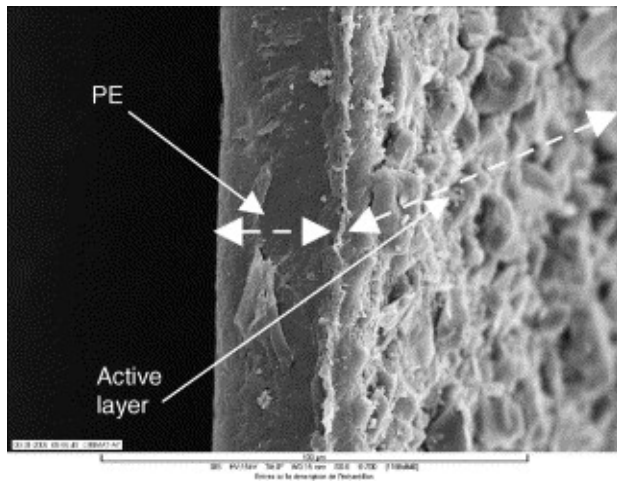

Fig. 13. MEB image of interface PE (left)—active layer (right) Sample of 50 wt% CNTs content.

The adhesion between the PE and the active layer is excellent and the hybrid capacitors are as flexible as the thin film of PE. The interpenetration is so achieved.
Fig. 14 presents a cross section with a tilt angle of 15° of PE—interface metallization. The interface is located at the intersection of two arrows in dotted lines. The metallization and the PE are located, respectively, on the left and on the right side of this intersection.
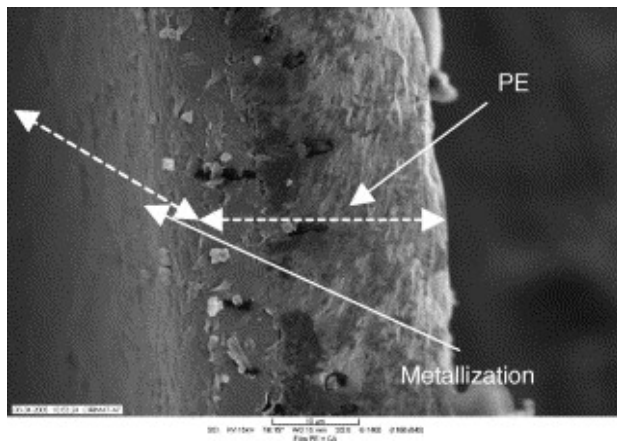

Fig. 14. MEB image of interface metallization (left)—PE (right) Sample of 50 wt% CNTs content.

The PE—interface metallization is relatively smooth.
These SEM pictures show that the surface at the interface 'electrode/dielectric material' has been increased due to the roughness of active layers and to the adhesion between PE and carbonaceous layer as compared with the other smooth interface.

5. Conclusion

In this paper, the simulation is the first tool used to determine the impact of surface roughness on the capacitance. As expected, it is showed that the capacitance increases with the surface roughness and this is all the more so true since dielectric thickness is small. Due to the rough and disordered surface, the distribution of the electric field is inhomogeneous: it leads to a non-linear change of the capacitance with the geometrical parameters. Finally, the increase of the capacitance value is more marked when the dielectric thickness is in the order of magnitude of roughness.

The realization of electrodes presenting a surface roughness using porous conductive nanomaterials such as activated carbon and CNTs has been undertaken. It leads to capacitance values, which increase with the surface roughness. Experimental results showed that the useful surface is the surface impregnated or accessible to the dielectric material and not the whole surface developed by the electrodes. The CNTs content plays a key role in the accessibility of the surface developed by the electrodes. Capacitance enhancement of 100% may be achieved. Nevertheless, with this technology, the realization of hybrid capacitors remains difficult. The key point in some cases remains the impregnation of the dielectric material. Results ought to be better with two rough electrodes than using only one rough electrode, but the mechanical pressure applied during the manufacture seems to limit the dielectric accessibility. Vacuum could be an alternative way to use two rough electrodes without performances degradation. These results will be presented in a future paper.

The using of many dielectric thicknesses will be interesting to confirm the non-linear dependence of the capacitance with the opposite dielectric thickness such as it is showed using the simulation. Works are still in progress to solve these different problems and to test this new type of components from an electrical point of view.

References

[1] Rajendra M. Patrikar, Chong Yi Dong and Wenjun Zhuang, Modelling interconnects with surface roughness, *Microelectronics Journal* **33** (2002), pp. 929–934.

[2] Y.-P. Zhao, G.C. Wang and T.M. Lu, Surface-roughness effect on capacitance and leakage current of an insulating film, *Physical review B* **60** (1999) (12), p. 2.

[3] G. Palasantzas and J.Th.M. De Hosson, The effect of mound roughness on the electrical capacitance of a thin insulating film, *Solid State Communications* **118** (2001), pp. 203–206.

[4] A.M. Madhy and H.I. Anis, Electrode Roughness Effects on the Breakdown of Air-insulated Apparatus, *IEEE Transactions on Dielectrics and Electrical Insulation* **5** (1998) (4).

[5] Yong-Kyu Yoon, Mark Allen, Tunable ferroelectric capacitor with low-loss electrodes fabricated using reverse side exposure, 53rd EMTC May 27, 2003.

[6] E. Flahaut, R. Bacsa, A. Peigney and Ch. Laurent, Gram-scale CCVD synthesis of double-walled carbon nanotubes, *Chemical Communication* (2003), pp. 1442–1443.

[7] Y.K. Jun, The fabricated and electrical properties of modulated stacked capacitor, *IEEE* (1992).

Corresponding author. Tel.: +33 5 61 55 82 42; fax: +33 5 61 55 64 52.