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Influence of carbonaceous electrodes on capacitance and breakdown voltage for hybrid capacitor

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Abstract

This paper presents a new type of capacitor and deals with a hybrid approach where the advantages of two systems, dielectric capacitors and the ultracapacitor are combined. The objective is to increase the capacitance and the energy storage capability, while or at least preserving or decreasing the volume of the passive components. In this aim, the surface area and structural properties of ultracapacitor electrodes and the high dielectric strength of a polymer material are associated. The surface roughness of the carbonbased electrodes, namely (activated carbon—AC, and carbon nanotubes—CNTs), has a good impact on the capacitance. However, the surface roughness also depends on the composition of carbonaceous materials and so does the capacitance. Moreover, the choice of the dielectric material is the key parameter. The better the impregnation of the roughness is, the better is the increase of the capacitance.

Since the final objective is to improve the electrical energy stored by the capacitor, the effect of surface roughness on the breakdown voltage is also evaluated.

Keywords: Dielectric capacitor; Surface roughness; Activated carbon; Carbon nanotubes; Roughness accessibility; Breakdown voltage; Electrical energy storage; Parylene; Polyethylene

1. Introduction

The context of this study is the integration of passive components and the miniaturization of electronic components. As for active components, the volume of passive components such as resistor, capacitor and inductance has to be downsized. Materials and their physical parameters must be reconsidered to find technology processes allowing a real modification of the size of the components while preserving or enhancing their electrical performance. The impact of the surface roughness on the capacitance values has already been published [1–5]: hybrid polyethylene (PE) capacitor realized by the association with the PE and carbonaceous electrodes of ultracapacitor [1] has been demonstrated an increase of 100% of the hybrid capacitor value compared with a capacitor with plane electrodes.

This capacitor consists in covering the carbonaceous electrode surface (active layer) with a PE film. The sample is then put in a drying oven at 130 °C during 5 min. After cooling the sample, a gold metallization coating is sputtered on the outer layer of PE. This second electrode or upper electrode surface area is 0.07 cm². The composition of the active layer affects the value of the capacitance: the larger rate of carbon nanotubes (CNTs) is, the larger is the capacitance. This result is explained by an increase of the accessibility of the dielectric material to the surface roughness. A simulation showed interesting results since the influence of the dielectric thickness on the capacitance was characterized. When the thickness decreased, the electrical field increased, leading to higher capacitance values.

In this paper, two different materials are investigated. The influence of the dielectric material nature is tested. Hence, PE capacitors are elaborated using following a solid route, whereas the capacitor fabrication by a gaseous route, through the deposition of another polymer: the

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parylene. This paper is organized in two parts. The first part presents the elaboration (through the gaseous route) and the characterization of the hybrid capacitor using a parylene deposited film as dielectric; the second part is devoted to the PE hybrid capacitor elaboration and characterization, for different thicknesses, to determine both the influence of the carbonaceous composition and of the variation of the breakdown voltage with the surface roughness. Finally, in order to find the best dielectric/conductor couple, to reach high capacitance values for the hybrid capacitor, the stored electrical energy is calculated and discussed. The experimental results are compared with those obtained by computing simulation.

1.1. Hybrid capacitor using parylene: vapour deposition process

Parylene, unlike other polymeric materials is produced by vapour-phase deposition and polymerization of paraxylène (or its substituted derivatives). These coatings provide excellent corrosion resistance, barrier properties and exhibit superior dielectric protection [6–8]. The most important characteristic of parylene is that the solid transformation from the gaseous phase occurs at room temperature giving a conformal coating that can be applied to a wide variety of substrates.

1.1.1. Process deposition of parylene

Commercially available parylene can be divided into three types N, D and C; type C is well known for its excellent electrical properties, like a dielectric strength of 500 kV mm^{-1} and a dielectric permittivity of 3.15, 3.10 and 2.95, respectively, at 100 Hz, 1 kHz and 1 MHz.

The parylene deposit is achieved through a three-step process: vaporization of the solid dimmer at $110\text{--}150^\circ\text{C}$ (no liquid phase). Pyrolysis of the dimmer vapours at 650°C (to transform them in a reactive vapour monomer). Polymerization takes place during deposit on the carbonaceous surface (the monomer being placed in a vacuum chamber (0.1 Torr) at ambient temperature).

1.1.2. Preparation of samples

Active layers are prepared through mixing of activated carbon (AC) powders (PicactifBP100 from the PICA Company, Vierzon, France) and of polytetrafluoroethylene (PTFE, from Dupont de Nemours) as binder. The active layer composition is $x \text{ wt}\%$ AC, $y \text{ wt}\%$ CNTs and 5% PTFE, with $x + y = 95$. The CNTs content for layers the different of active materials are 0, 30, 50 and 100 wt%. Once processed under film, they are stucked to a planar metallic support thanks to a silver paste. Fig. 1 shows a SEM image of a sample of an active layer with 50 wt% CNTS–50 wt% AC. This metallic support constitutes the first electrode while the second electrode is the gold metallization realized once the parylene film deposition has been achieved. Several metallization zones ($S = 1.28 \text{ cm}^2$) are randomly realized onto the paralyene

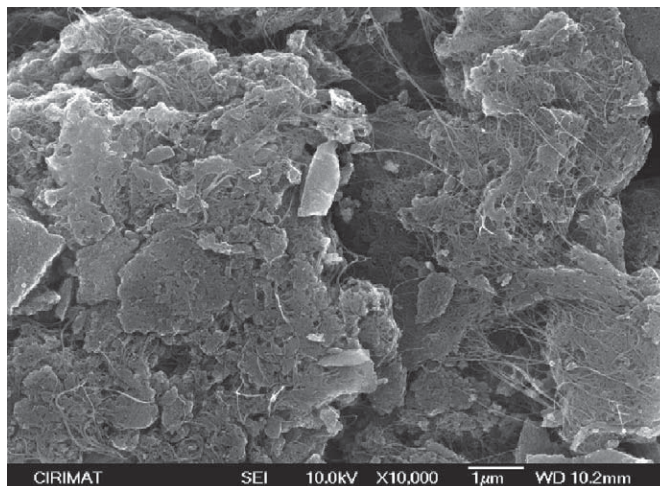


Fig. 1. SEM image of a sample of an active layer with 50 wt% CNTs.

film to collect multiple data for each sample. It is a proof that on one hand the lowest size of porosity is not accessible and, on the other hand that lost, different parylene thicknesses have been tested: 10, 20 and $40 \mu\text{m}$.

1.1.3. Contribution of CNTs to the surface roughness

Impregnation of the carbonaceous surface by the dielectric material is the key parameter. The challenge is to obtain a surface of contact between the dielectric and the electrode which presents the highest value. Previous works have already presented the interest of adding CNTs to the carbonaceous composition (generally based on AC) [1,9], since they improve the surface accessibility for the dielectric. Indeed, even if the specific surface area of the AC is around from 1000 to $1500 \text{ m}^2/\text{g}$ whereas for CNTs, it is $500\text{--}600 \text{ m}^2/\text{g}$, the roughness accessibility is higher when the CNTs content in the electrode is increased. CNTs agglomerate together offering a roughness of an appropriate size.

1.1.4. Electrical tests: capacitance values

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). Parylene-based capacitors are measured at 10 kHz and 1 V. Figs. 2a–c present the capacitance values versus the carbonaceous composition for 10, 20 and $40 \mu\text{m}$ parylene film thickness.

These electrical results are interesting: they confirm that the capacitance values increase when using carbonaceous electrodes. Whatever the thickness of the parylene, the capacitance is 20–40% higher, compared with a plane capacitor of a capacitor using 100% NTCs. There are however some drawbacks with this type of capacitor.

This phenomenon is not observed for the others types of coatings, contrary to the results presented in [1]. The low dispersion of the capacitance values, due to the difficult process of carbonaceous layers was the most likelihood explanation.

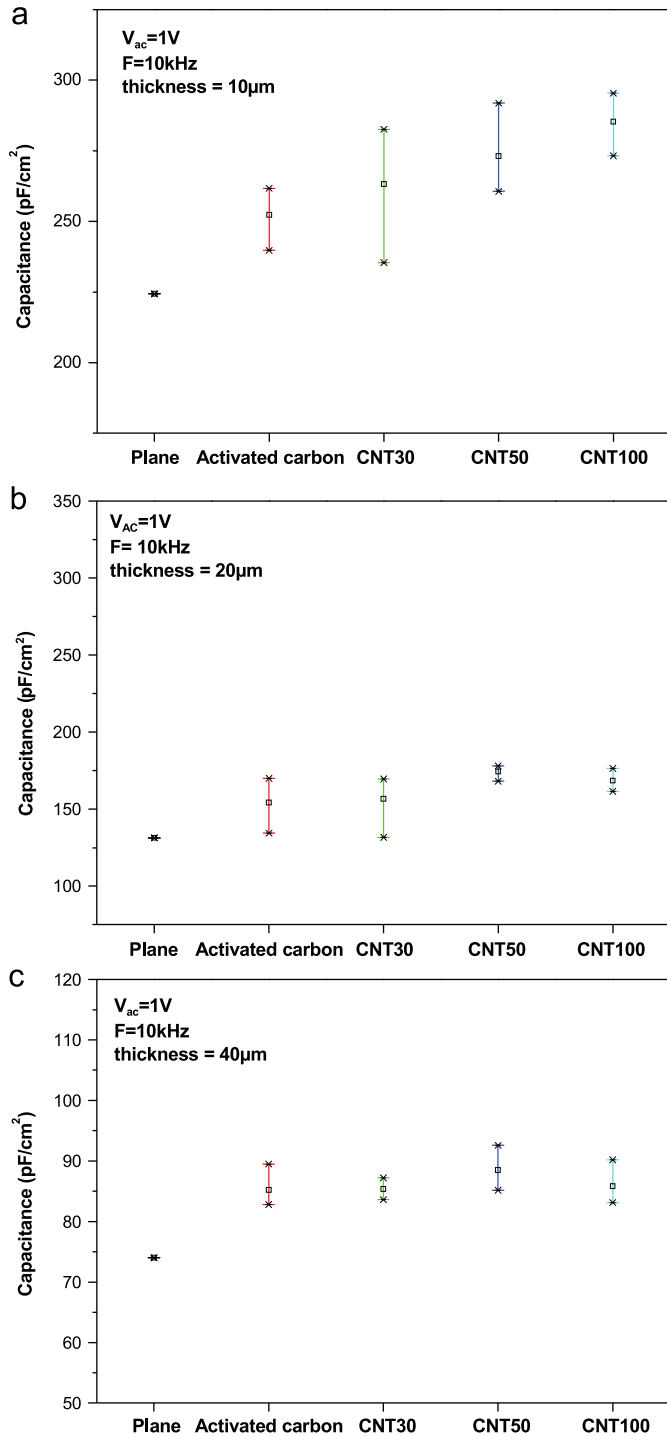


Fig. 2. (a) Capacitance values versus carbonaceous composition for a thickness of $10\mu m$ of parylene, for five electrodes types. (b) Capacitance values versus carbonaceous composition for a thickness of $20\mu m$ of parylene, for five electrodes types. (c) Capacitance values versus carbonaceous composition for a thickness of $40\mu m$ of parylene, for five electrodes types.

When the CNTs content increases, the process for the realization of the layer becomes more and more difficult. It is therefore not easy to conclude to the influence of the dielectric thickness on capacitance values.

On the other hand, a poor increase of the capacitance is observed. Parylene is known to lead to conformal coating of a complex surface, which would lead, for the electrodes under study to high capacitance values. Parylene deposits have been observed using SEM. Figs. 3a–d show images of a $40\mu m$ parylene coating for, respectively, 100% AC, 30–70% CNTs-AC, 50–50% CNTs-AC and 100% CNTs electrodes. First, from Fig. 3a–c, the effect of increasing the roughness is more and more marked: it means that the best impregnation of the parylene is achieved with 100% CNTs content. However, some large particles, whose sizes are not consistent with the thickness of $10\mu m$ are observed, maybe due to a too fast deposition rate. Such a result may be one of the reasons of the poor capacitance values obtained.

1.2. Hybrid capacitor using polyethylene: the solid route

The experimental process used to realize a PE hybrid capacitor has already been described [1]. In this study, it was shown that the insertion of a PE film of $40\mu m$ led to a capacitance of $100 pF/cm^2$ for the hybrid capacitor as compared with the $50 pF/cm^2$ obtained for the planar which represents an increase of 100%. Hence, the impact of the PE film using different film thickness is studied. These experimental results will be compared with theoretical data obtained using a computing simulation method.

1.2.1. Capacitance values of $15\mu m$ capacitor

Capacitances are measured for the same experimental way. Fig. 4a and b show the capacitance for different carbonaceous electrode compositions (0 wt% carbon, 100 wt% AC, 50–50 wt% AC-CNTs and 100 wt% CNTs), for two different film thicknesses, 40 and $15\mu m$. For the former thickness (Fig. 4a), the capacitance increases of about 12% for 100 wt% AC, 40% for 50–50 wt% AC-CNTs and 100% for 100 wt% CNTs contents. For the later (Fig. 4b), the increase of the capacitance is more marked for 100 wt% contents AC rather than $40\mu m$ (55%). It is about 85% for 50–50 wt% AC-CNTs.

Hence, for the same electrode composition, the capacitance improvement is more important when using a PE film of $15\mu m$ rather than a film of $40\mu m$, except for the 100% CNT electrodes. This result is surprising since an increase of 100% was expected. A simulation work has to be carried out in order to answer this question.

1.2.2. Simulation

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

$$C = \epsilon_0 \epsilon_r S / e. \quad (1)$$

When the surface roughness increases, the local conditions of the electric field become unknown; the classical

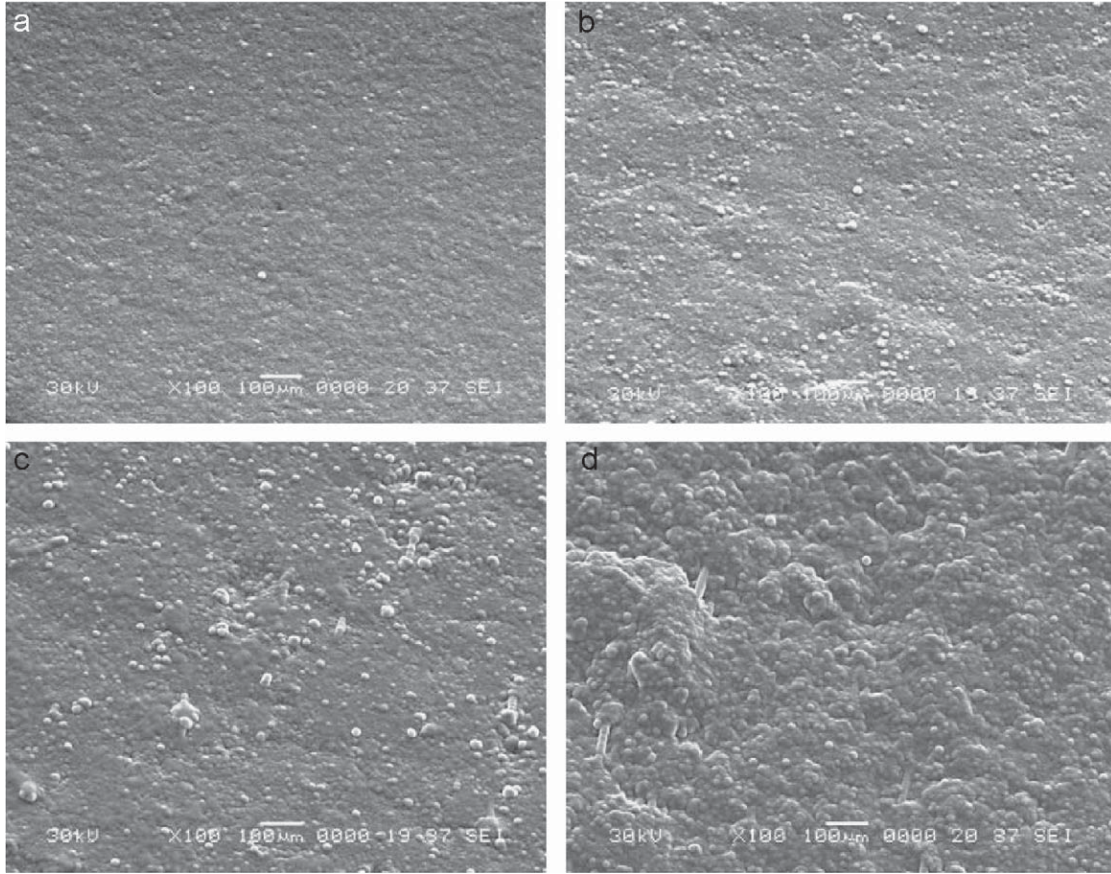


Fig. 3. (a) SEM image of parylene deposition (10µm/100% activated carbon) (100). (b) SEM image of parylene deposition (10µm/70–30% activated carbon-CNTs) (100). (c) SEM image of parylene deposition (10µm/50–50% activated carbon-CNTs) (100). (d) SEM image of parylene deposition (10µm/100% CNTs) (100).

analytic formulation (1) of the capacitance is not more suitable. It is however possible to calculate the capacitance values from the density of the electrical energy using finite element method [5]. In our case, using a simple but representative geometry for the rough and disordered surfaces (teeth of saws, see Fig. 5), the capacitance values is calculated from the distribution of the density of the electrical energy U_e (J m^{-3}) according to (2).

$$U_e = \frac{1}{2} CV^2. \quad (2)$$

Different geometrical figures are proposed to compare variable specific surfaces (Fig. 5). The surface roughness is characterized by the number of teeth per unit of length: there are six teeth for the lower electrode. Note that the depth of teeth is identical in all geometrical figures, allowing to define an average plane thickness “ e ” located on the middle height of these teeth. The width of every plane represents the average dielectric thickness. Geometrical dimensions are in arbitrary units: capacitance values are reported in these arbitrary units and the depth of teeth is 0.2.

Four geometries are presented in Fig. 5. A perfect impregnation is achieved when the dielectric fully covers the carbonaceous surface; as a consequence, this surface area is fully reported on the upper electrode (Fig. 5,

electrode design “A”). On the other hand, due to the physical properties of dielectric or to the specific interaction with the carbon surface, the impregnation may not be complete. Some changes in the dielectric thickness are observed; represented in Fig. 5, design “B”. Then, the “C” case, represents a surface without roughness on the upper electrode. The capacitor with plane electrodes (lower and upper) is represented by the design “D”.

Fig. 6 shows the normalized capacitance change versus the dielectric film thickness. “A” design leads to a real increase of the capacitance with a thin dielectric film thickness. The change of the capacitance for the planar design (“D”) is linear whereas it is not the case for the others, showing the influence of the surface roughness in a qualitative way.

When compared with experimental results, the ideal “A” design is not experimentally obtained. However, using 40 and 15 µm thick PE films, leads to increase the capacitance values. PE does not impregnate the whole surface (the surface of the lower electrode is not totally reported on the upper electrode), which would explain the relative increase of capacitance. The design “B” appears to be the most valuable representation of the dielectric PE film/carbonaceous electrode interface in the experimental hybrid PE capacitor.

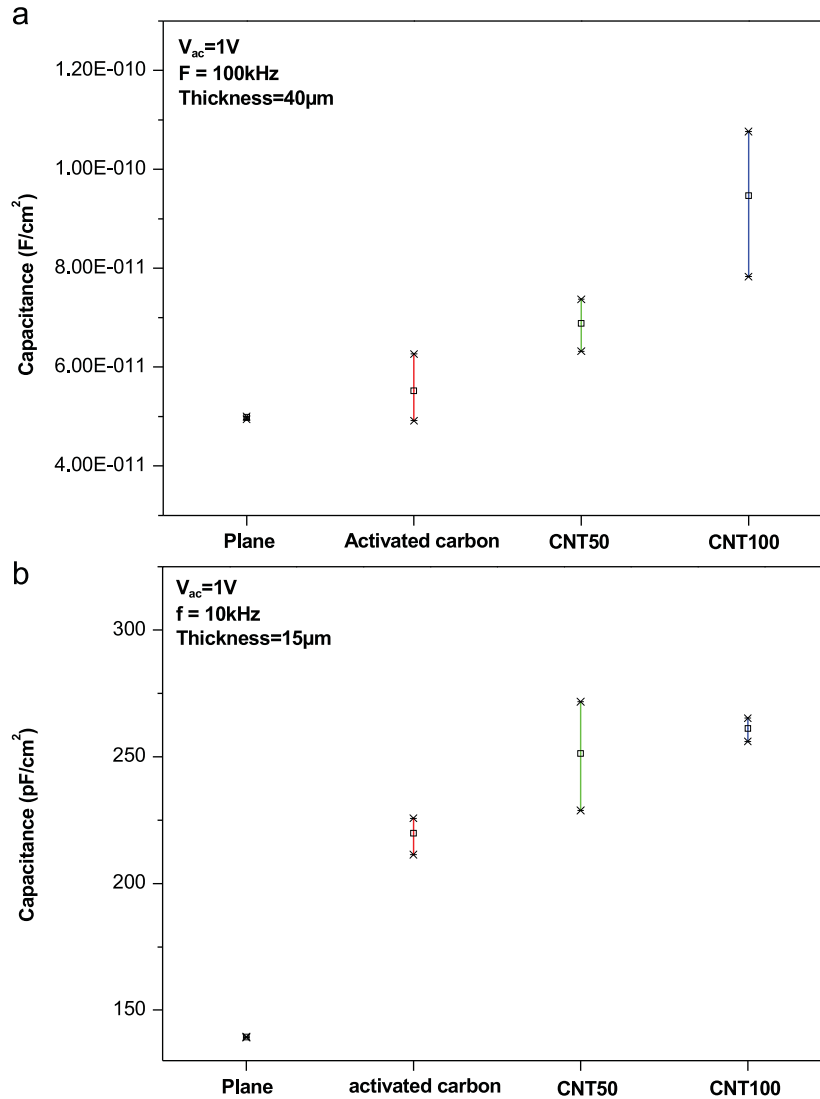


Fig. 4. (a) Capacitance values versus carbonaceous composition for a thickness of 40 μm of polyethylene, for four electrodes types. (b) Capacitance values versus carbonaceous composition for a thickness of 15 μm of polyethylene, for four electrodes types.

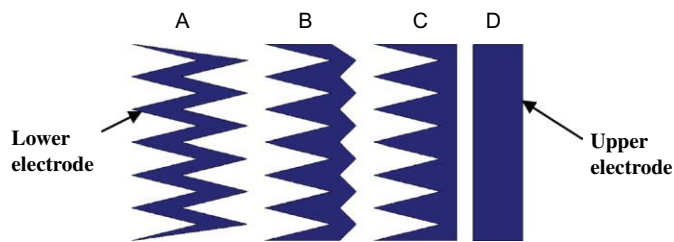


Fig. 5. Geometrical figures used for the simulation. Electrodes are represented by outlines (Voltage = 10V) and the dielectric material is represented by black areas ($\epsilon_r = 3$).

1.2.3. Breakdown voltage of hybrid polyethylene capacitor

The capacitance values are doubled in the case of the hybrid PE capacitor assembled with 40 μm of PE, compared with the plane capacitor. According to (2), the electrical energy depends of the square value of the voltage. The determination of the breakdown voltage (dielectric strength) must be determined in order to appreciate

electrical energy stored by the hybrid capacitor. Samples presenting a dielectric whose thickness range between 15 and 40 μm , with same carbonaceous composition are tested. Capacitance values are reported in Table 1 for 40 μm and in Table 2 for 15 μm .

The sample is placed between two electrodes to measure the breakdown voltage. One electrode is in contact with the metallized surface of 0.07 cm^2 . Four compositions of carbonaceous electrodes are tested: 0 wt% carbon, 100 wt% AC, 50–50 wt% AC-CNTs and 100 wt% CNTs. Four samples are tested for each composition.

Whatever the PE thickness, the breakdown voltage decreases when carbonaceous materials constitute the electrodes of the capacitor. Hence, the breakdown voltage was around 9 kV. It is divided by 3 whatever the carbonaceous composition. The influence of the surface roughness on the local reinforcement of the electrical field is evidenced. The same trend is observed for 15 μm : the value of 4.5 decreases down to 1.2 kV in the same

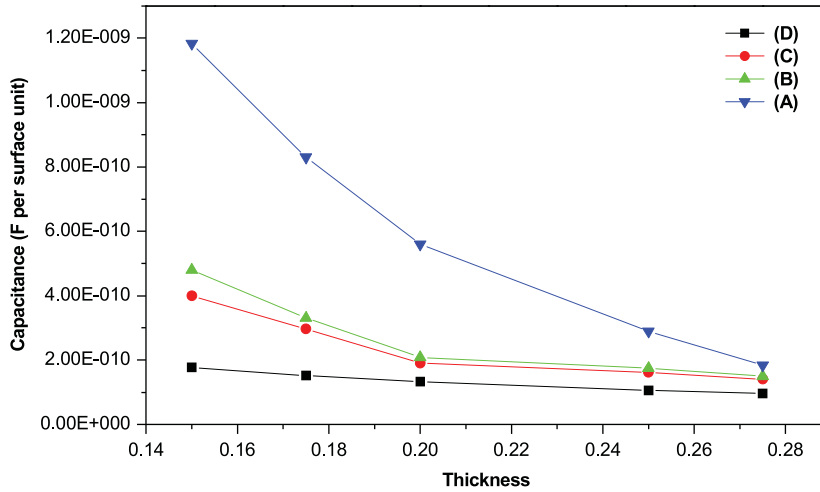


Fig. 6. Capacitance values (normalized) versus thickness for a given form (A, B, C or D).

Table 1
Breakdown voltage (kV) of hybrid polyethylene capacitor of 40 μm of polyethylene for four electrodes types

	Sample 1	Sample 2	Sample 3	Sample 4
Plane	9.03	9.3	9.5	9.1
100 wt% activated carbon	3	3	3.03	3.3
50–50 wt% activated carbon-CNTs	3.03	3.1	3.2	3.01
100 wt% CNTs	3.8	3.7	3.9	3.6

Table 2
Breakdown voltage (kV) of hybrid polyethylene capacitor of 15 μm of polyethylene for four electrodes types

	Sample 1	Sample 2	Sample 3	Sample 4
Plane	4.5	4.5	4.5	4.5
100 wt% activated carbon	1.78	1.22	1.2	0.24
50–50 wt% activated carbon-CNTs	1.13	2.24	0.7	1.10
100 wt% CNTs	1.49	1.24	1.2	1.06

conditions. Note that the breakdown voltage values are homogenous from a sample to another, which means that the increase of the surface roughness between 100 wt% AC and 100 wt% CNTs is not the main cause but only the accessibility to the surface roughness, which is better.

Since, the final objective is to obtain a dielectric capacitor with strong energy storage, Tables 3 and 4 present the electrical field stored by plane capacitor and hybrid capacitor for 40 and 15 μm of PE, respectively. These results show that despite the improvement of the capacitance of the hybrid capacitor, the decrease of the breakdown voltage leads to a lower electrical energy

Table 3
Electrical energy (J per surface unit) of hybrid polyethylene capacitor of 40 μm of polyethylene for four electrodes types

	Sample 1	Sample 2	Sample 3	Sample 4
Plane	2.025×10^{-3}	2.10×10^{-3}	2.025×10^{-3}	2×10^{-3}
100 wt% activated carbon	2.6×10^{-4}	2.8×10^{-4}	2.7×10^{-4}	2.7×10^{-4}
50–50 wt% activated carbon-CNTs	3.15×10^{-4}	2.8×10^{-4}	2.9×10^{-4}	3.17×10^{-4}
100 wt% CNTs	4.8×10^{-4}	4.4×10^{-4}	4.4×10^{-4}	3.6×10^{-4}

Table 4
Electrical energy (J per surface unit) of hybrid polyethylene capacitor of 15 μm of polyethylene for four electrodes types

	Sample 1	Sample 2	Sample 3	Sample 4
Plane	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}
100 wt% activated carbon	3.5×10^{-4}	1.5×10^{-4}	1.6×10^{-4}	6.3×10^{-4}
50–50 wt% activated carbon-CNTs	1.7×10^{-4}	6.5×10^{-4}	5.6×10^{-4}	1.5×10^{-4}
100 wt% CNTs	2.9×10^{-4}	2×10^{-4}	1.98×10^{-4}	1.4×10^{-4}

stored. However, these hybrid capacitors can be used in many applications: since, it stays relatively important (1.2 kV for 15 μm and 3 kV for 40 μm).

2. Conclusion

Hybrid capacitor constituted by a gaseous process is used for the deposition of dielectric material have been realized. Parylene coating is achieved on top of carbonaceous electrodes. This material is claimed to allow a conformal coating. Regarding the electrical properties, the maximal increase is 40% for this material: SEM images

showed some defects on the surface of the deposition, which involve thickness variability. For the thickness of 10 μm of parylene, the influence of the composition of the carbonaceous electrode is better than with others thicknesses: increasing the rate of CNTs leads to an increase of the accessibility to the surface.

Another elaboration route has also been investigated. It consists in using polymer films of PE and process them. An increase of 100% of the capacitance is observed for 40 μm . However for a PE of 15 μm , capacitance values are increased but not in the proportions expected.

Hybrid capacitor with a thickness of 40 μm had to be considered as the reference since it is the best demonstration of the improvement of the capacitance value and it is easy to process PE.

The breakdown voltage of PE hybrid capacitors is measured for two thicknesses 40 and 15 μm . For both of them, the breakdown voltage decreases with carbonaceous surface compared with a plane electrode. The calculation of the electrical energy stored by the hybrid capacitor shows that the increase of the capacitance values is not sufficient to obtain the same level than the one of a plane capacitor, whatever the thickness of PE film.

Works are still in progress to increase the compatibility between the dielectric material and the carbonaceous film and to realize the process adapted to these materials. Moreover, the study is concentrated from an energy point of view. It would be interesting to analyse other criteria like ESR, thermal behaviour of the hybrid capacitor.

One of the most promising perspectives would be to elaborate carbonaceous electrodes by the growth of carbon nanotubes on a metallic support and to control the roughness.

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