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COMPACT, INTERDIGITATED CONSTRUCTAL DESIGN APPLIED TO SUPERCAPACITOR SYSTEMS

Alexandru M. MOREGA[1,2], Juan ORDONEZ[3], Mihaela MOREGA[1], Lucian Pîslaru-Dănescu[4], Alin A. DOBRE[1]

[1] "Politehnica" University of Bucharest, 313 Splaiul Independentei, Bucharest, 060042, Romania
[2] "Gheorghe Mihoc – Caius Iacob" Institute of Mathematical Statistic and Applied Mathematics, Romanian Academy, 125 Calea Victoriei, Bucharest, 010071, Romania
[3] Florida State University, Tallahassee, FL 32310, USA
[4]National Institute for Research and Development in Electrical Engineering ICPE-CA, Bucharest, Romania
Corresponding author: Alexandru M. MOREGA, E-mail: amm@iem.pub.ro

Abstract. Interdigitated grid topology may provide for higher quality electrical devices, which are sieges of electric and magnetic fields, in terms of capacity, reconfiguration capability, and compactness. It is then important to provide design solutions that add to these the architectural scalability required to produce readily available solutions for designers. This paper aims to propose a constructal solution for interdigitated grid topologies based on an optimal scalable, minimum-redundant, reconfigurable interdigitated topology for planar electric devices. Although the interdigitated constructal design (ICD) may be of interest in the optimization of numerous planar structures, here we envisage two applications. In this paper, ICD is applied to optimize a planar micro supercapacitor that utilizes vertically grown carbon nanotube forests electrodes. This study relies on numerical solutions to boundary value problems that are solved using the finite element method.

Key words: Constructal law, Optimization, Supercapacitor, Carbon nanotubes forests, Interdigitated electrodes, Numerical simulation.

1. INTRODUCTION

Supercapacitors (SCs) are electrolytic capacitors with enhanced electrical charge storage capacity [1]. As their dielectric is an ion-conducting electrolyte, under a biased voltage, positive and negative ions separate and accumulate by the electrodes surfaces, producing the nm-thin electro-chemical double layer (EDL). The EDL ionic segregation and migration produce two capacitors connected in series [2].

The SCs with carbon nanotubes electrodes (SCNTs), unlike regular electrolytic capacitors, use extremely porous electrode materials to enhance the interfacial capacitance. The electrolyte/porous electrodes interface enhance the EDL phenomenon to astonishingly high value of specific capacitance (capacitance per unit area) [3]. When compared to fuel cells and Li-ion batteries, the charging/discharging process of the SC, which imply no chemical reaction, their stable performance (~106 cycles vs. ~103 cycles of Li-ion batteries [1]) and less temperature dependency, are of particular importance in medium and small power applications like vehicle regenerative braking and as the main power sources for short-term, high power-density usages in many applications. SCs are envisaged also as reversible power sources in pulse-power applications such as MEMS solid-state sensors, and for temporarily energy storage from energy harvester and power the system for sensing and wireless communication needs.

Enhanced electrodes structures were investigated, *e.g.*, conducting polymer-coated metal layer [4] electrodes, KOH etching to increase the electrodes surface area [5], carbon nanotubes (CNT) with high surface area-to-volume ratio and good conductivity deposited on the electrodes [6], CNT arrays transferring to a conductive substrate after the synthesis process [7]. Recently, planar architectures with nanotube (CNT) forests are utilized as electrodes in SCs.

Here we apply the *Constructal Law* (CL) method [8] to enhance the performances of planar SCs with interdigitated finger electrodes configuration: systems of finite volume with internal fluxes (currents) that may cross their boundaries and which are subject to internal and external constraints morph such that their shape and structure facilitate easiest access to fluxes. This is true for animate and inanimate systems in Nature. In the engineer realm, systems are designed to meet this request optimally. Here we use this prediction for a supercapacitor system with porous, carbon nanotubes electrodes (SCNT).

The study is concerned with the constructal design of interdigitated electrodes SCNT, with optimal static capacitance and stationary electrical resistance. For transient working conditions, the physical model has to depart the static (for capacitance) and stationary (for resistance) assumptions, the external load to the SCNT has to be considered, therefore some adjustments to the optimal design evidenced here may occur. The analysis of dynamics impact upon the SCNT structure and shape makes the object of a future research.

2. THE MATHEMATICAL MODEL

In the first stages of the design, for analysis and measurements purposes, simpler working conditions for the SCNT may be utilized. For instance, its capacitance may be computed and measured using static working conditions, whereas its electrical resistance can be characterised using electrokinetic conditions. The mathematical models that describe these particular regimes are presented next.

Supercapacitors use electrolytes as dielectric medium. The contact electrode – electrolyte leads to the formation of an electrical double layer (EDL) made of a layer of electrons in the electrode (if the electrode is a metal or electronic conductor), on one hand and a layer of adsorbed ions and a diffuse, ionic cloud, on the other hand. The ions in the diffuse double layer of sign opposite to the electrode surface are present in excess compared to the bulk electrolyte. The EDL results into a fall of the electric potential and has a big impact on the analysis and simulation of supercapacitors.

Figure 1 provides a qualitative representation of the electrostatic voltage profile in the EDL, by the electrode-electrolyte interface. SCNTs, as all supercapacitors, show off this effect, and the intrinsic voltage drop on the EDL is part of the total voltage drop on the SCNT (for each armature). Moreover, in this study we are concerned with capacitors with symmetric electrolytes, whose formula unit has one cation and one anion that dissociate completely.

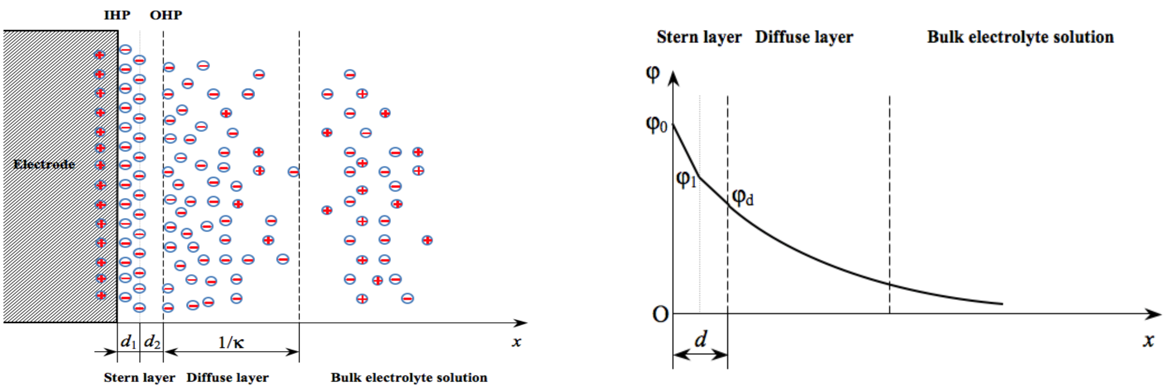


Fig. 1 – The electrical field (potential) inside the EDL: Helmholtz planes (the inner plane, IHP, and the outer plane, OHP), Stern layer, and diffuse layer – the Gouy-Chapman model (after [2]).

As the porous carbon matrix grown on top of the SCNT electrodes extends the metal – electrolyte contact, the theoretical maximum capacitance for the device can be computed using

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \tag{1}$$

where ε_0 is the permittivity of the vacuum, 8.854×10^{12} F/m, ε_r is the relative permittivity of the electrolyte, 11.7 for [BMIM][BF4][1] [10], $d = d_1 + d_2$ is the double-layer thickness, an electrolyte-dependent parameter too, 0.69 nm here [12, 13], and A is the overall surface area of electrodes.

The SCNT utilizes multiwalled carbon nanotubes with a diameter of ~30 nm, for which the surface to mass ratio is 110 m^2/g. The total active surface, A, may be estimated by using the mass of CNT forests of the

[1] 1-Butyl-3-Methylimidazolium Tetrafluoroborate [10, 11]

device. For instance, a mass of 3×10^{-5} g yields an area of 3.3×10^{-3} m^2. Moreover, the equivalent electrical circuit of a SCNT may be thought of as made of two capacitances connected in series, one for each of its armatures. Then, the theoretical value of A has to be divided by two, which yields 1.65×10^{-3} m^2. Using these derivations, eq. (1) may provide for the theoretical peak capacitance (*e.g.*, 248 μF), which is an upper limit [10].

Figure 2 shows a qualitative view of an electrode with CNT grown on top and filled with electrolyte, and its equivalent model proposed in this study.

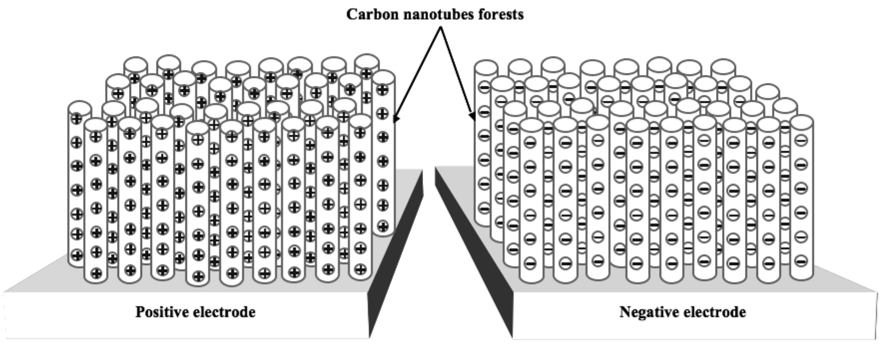


Fig. 2 – Qualitative sketch of carbon nanotubes electrodes. The electrolyte separates in positive and negative ions that build electrical charges layers by the electrodes.

We assume that the CNT forest and the filling electrolyte are replaced with a homogeneous block with anisotropic relative permittivity

–parallel to the CNT

$$\varepsilon_{\parallel} = \varepsilon_{CNT} + \varepsilon_{e}, \tag{2}$$

–perpendicular to the CNT

$$\varepsilon_{\perp} = \frac{\varepsilon_{CNT}\varepsilon_{e}}{\varepsilon_{CNT} + \varepsilon_{e}}, \tag{3}$$

where ε_{CNT} is the sheet CNT relative permittivity, and ε_e is the electrolyte relative permittivity. Here ε_{CNT} = 1.3 and ε_e = 11.7 [12].

The electrostatic field inside the SCNT, outside the EDLs that exist by the electrodes, is described by

$$\Delta V = 0, \tag{4}$$

where V [V] is the electrostatic potential.

The boundary conditions that close the mathematical model are electrical insulation (zero charge) everywhere, except for the electrodes, where Dirichlet (potential) conditions are assumed. Here V_+ = 100 mV and V_- = –100 mV.

2.1. The electrokinetic field

In stationary working conditions, the electrical field is described by

$$\Delta V_k = 0, \tag{5}$$

where V_k [V] is the electrokinetic potential. Here too, it is convenient to approximate the carbon forest and the electrolyte inside it with a homogeneous block with anisotropic electrical conductivity that yields

– parallel to the CNT

$$\sigma_{\parallel} = \frac{\sigma_{CNT}\sigma_{e}}{\sigma_{CNT} + \sigma_{e}}, \tag{6}$$

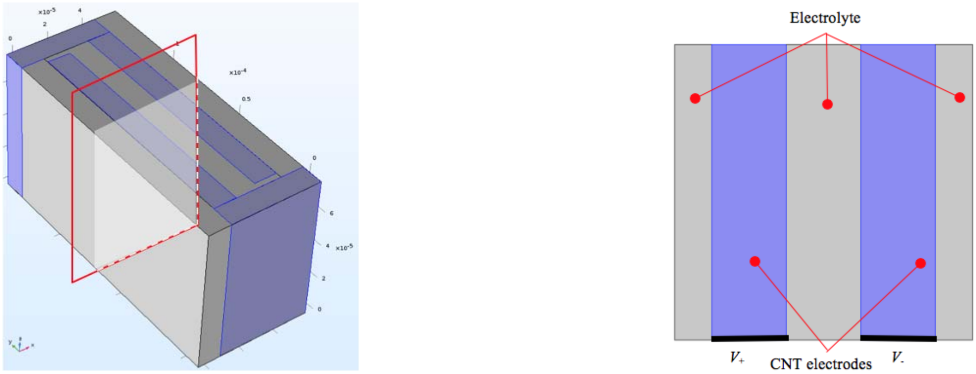
– perpendicular to the CNT

$$\sigma_{\perp} = \sigma_{CNT} + \sigma_{e}, \tag{7}$$

where s_{CNT} is the sheet CNT conductivity, and σ_e is the electrolyte conductivity. Here s_{CNT} = 100 S/m and σ_e = 0.1 S/m [10]. The mathematical model (1)-(7) is solved using the finite element method (FEM) [13].

THE ELEMENTAL CELL

Figure 3 presents the elemental cell initial shape and structure, the first construct in the optimisation sequence on the way to find the optimal structure and shape that provide for high capacitance, high resistance, and short characteristic time. As the length of SCNT finger-type electrodes is much larger than the cross-sectional dimensions therefore a 2D analysis in a plane orthogonal to the finger may outline conveniently yet accurately the main features of the electrostatic and electrokinetic fields inside the SCNT.



a b

Fig. 3 – The elemental cell (dimensions are in meters): a) the elemental SCNT; b) cross-sectional *x*O*z* plane.

In the optimization sequence, it is assumed that the area of the cell is kept constant (6 400 μm^2), as are the areas of the CNT (3 200 μm^2) and electrolyte (3 200 μm^2) blocks too.

Figure 4, a shows the results of the parametric study that outline the capacitance of the elemental cell as function of the cell shape factor, *H*/*L* (height/length). The CNT block is divided in 1…4 pairs, connected in parallel to the positive and negative terminals respectively. For each case, there exists an optimal aspect ratio. In computing the capacitances values, the CNT finger length is taken 80 μm.

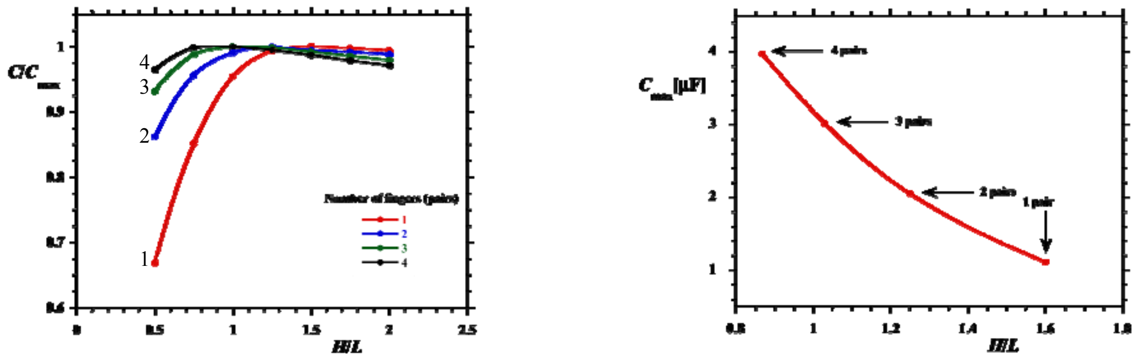


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Fig. 4 – The first optimization sequence: a) the capacitances are divided through their maximum values for each case (number of pairs of CNT blocks); b) the maximum capacitance as function of the number of CNT blocks.

Figure 4b presents the maximum capacitances values for the number of CNT blocks.

The maximum capacitance increases with the number of CNT, for decreasingly aspect ratio. In fact, the CNT f1orests only as tall as 100 mm are commonly available, and this is a limiting factor in the construction of SCNT that may cut off the optimization sequence. Figure 5a presents the resistance of the elemental cell as function of the geometric aspect ratio (AR). Unlike the capacitance, the resistance shows off a monotonic, decreasing variation with increasing AR. Apparently, the smaller the resistance the better for the SCNT as the ohmic losses are proportional with it. So, the selection of a SCNT with specific AR is a trade-off decision between high electrical energy storage capacity (high capacitance) and acceptable pending ohmic losses. Of course, energy storage is the main function of the SCNT. However, as seen, ohmic losses are of concern too, and further more.

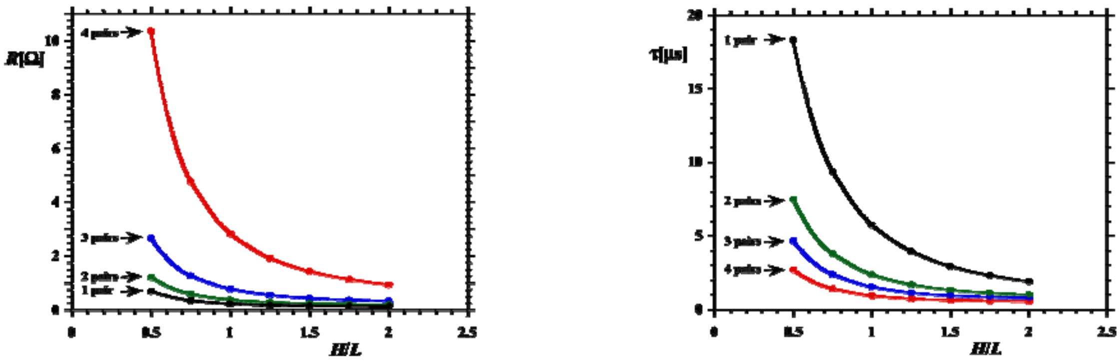

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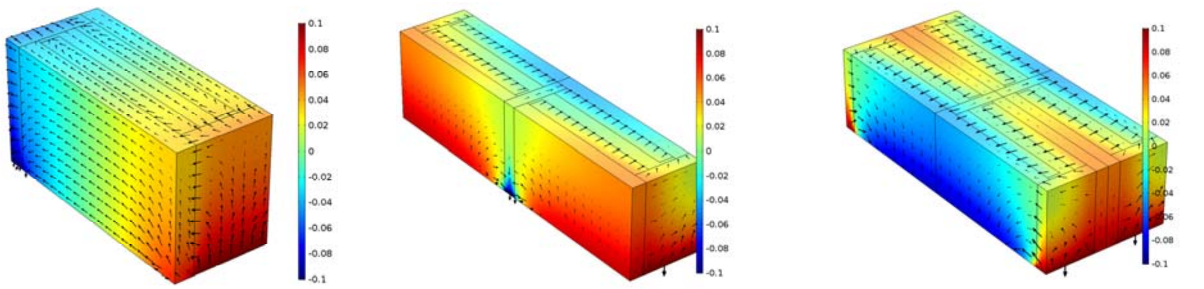
Fig. 5 – The second optimization sequence: a) the resistance of the elemental cell as function of the number of CNT blocks; b) the time constant of the elemental cell as function of the number of CNT blocks, for the optimal elemental cell.

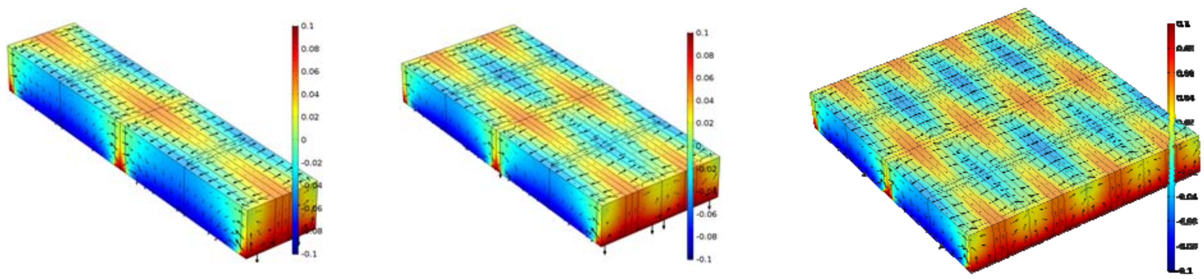
Another important criterion yet in selecting the optimal elemental cell is the time constant of the device, which is computed as $t = RC$ [s], Fig. 5b. Next, the optimal elemental cell, selected against on the three criteria (capacitance, electrical resistance, and time constant) is assembled to produce higher order ensembles.

4. HIGHER ORDER ENSEMBLES

Here we present the first four ensembles with interdigitated electrodes obtained by successive mirroring the elemental cell: the elemental cell, the resulting first order ensemble, the second order one, *a.s.o*. Figure 6 shows these constructs.



a. Optimized elemental cell b. Fist order ensemble c. Second order ensemble



d. Third order ensemble e. Fourth order ensemble f. Fifth order ensemble

Fig. 6 – The first six steps on the constructal sequence. The electric potential is in volts.

The electrostatic field is seen through surface colour map of electric potential, and arrows the electrical field strength, $\mathbf{E}$ = grad V [V/m]. The packaging strategy here, in fact, relies on successive parallel connections of lower order ensembles into higher order ensembles. It is worth mentioning that, thus, the capacitance doubles while the resistance divides by half for each growth step. This indicates geometric series, with 2, respectively ½ ratios. However, the time constant remains the same, *i.e.*, an *invariant* of this constructal entity.

5. CONCLUSIONS

The Constructal Law (CL) method is applied to improve the performances of planar supercapacitors with carbon nanotubes forest electrodes (SCNTs) and interdigitated finger electrodes configurations. The results of this study are useful in the first stages of the SCNT design, for analysis and measurements purposes, and it relies on modelling simpler working conditions.

Assuming that the CNT forest and the filling electrolyte are replaced with homogeneous blocks with anisotropic relative permittivity and electrical resistivity, a 2D analysis in a plane orthogonal to the finger outlines conveniently yet accurately the main features of the electrostatic and electrokinetic fields inside the SCNT. In the CL optimization sequence conducted on the 2D model it was assumed that the area of the SCNT cell, the area of the CNT, and that of the electrolyte blocks are constant, and that the cell geometric aspect ratio (AR) (height/length) is the single optimization variable. The capacitance as AR-function shows off a maximum, which singles out the optimal cell geometry. The maximum capacitance increases with the number of CNT, for decreasingly AR. The resistance varies monotonically (decreases) with AR, therefore the optimal cell shape should be a trade-off decision between a high storage capacity and conveniently high ohmic losses cell.Another important criterion yet in selecting the optimal elemental cell is the time constant of the device, which may be computed using the values of capacitances and resistances. Summing up, three criteria (capacitance, electrical resistance, and time constant) may be considered in selecting the optimal cell.

The packaging strategy presented here, in fact, relies on successive parallel connections of lower order ensembles into higher order ensembles. It is worth mentioning that, thus, the capacitance doubles while the resistance divides by half for each growth step. This indicates geometric series convergences with 2, respectively ½ ratios. However, the time constant remains the same, *i.e.*, *an invariant* of this constructal entity.

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