Sub-millimeter arbitrary arrangements of monolithically micro-scale electrical double layer capacitors

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Abstract. We report the investigation on the reproducibility of micro-scale electric double layer capacitors (micro-EDLCs). The micro-EDLC components were fabricated parallel using photolithography, wet and dry processing. Electrodes of the micro-EDLCs are highly dense packed Single Wall Carbon Nanotubes (SWCNTs) that form a mesh structure. The micro-EDLCs are connected 1-10 in series and in parallel being unified electrical circuits to tune the capacitance and the operational voltage. To confirm the reproducibility of the cells as well as the yield we performed electrochemical measurements in order to define the performance uniformity between cells strings and individual cells connected in a string. For 1-10 cells in series and in parallel the trends for the capacitance and operational voltage satisfied electro-physics rules governing cells addition. However, the measurements of the individual cells in a string revealed the significant performance discrepancy that might result in a shorten life cycling of a circuit.

1. Introduction
The trend in portable electronic devices have advanced by scaling down the electrical components, such as transistors, resistors and inductors, with the exception of Al electrolytic capacitors (AECs) which have remained on the centimeter-scale for the past 50 years. The obstacle in size shrinking lies in a restricted accessible area of the Al electrodes. Contrary, supercapacitors, based on the electric double layer to store the energy, offer energies approaching the level of batteries. However, their power is minor compared to the AECs due to the limited ions diffusion in an inner pore network of the activated carbon (AC) electrodes and a separator placed between an anode and a cathode. Recently, use of nanocarbonous materials (CNTs, graphene, carbon onion) together with high resolution techniques resulted in micro-supercapacitors with significantly improved speed because of shorten the ions diffusion path. The first has attained the improved accessible surface area for the electrodes, while the latter has been used to form planar, interdigital structures with an empty space instead of the separator. Parallel to the high power performance (two-order higher than supercapacitors) the micro-supercapacitors benefit of high capacitance, hence energy, becoming the potential candidate to replace the bulky AECs [1,2].
Recently, we developed the scalable and compatible process for the Integrated Energy Device Circuit (IEDC) that performance was similar to a target AEC but its volume differed 1 to 1000th in the size [2]. The IEDC was composed of the individual, similar micro-EDLCs. Each micro-EDLC worked as an independent electrochemical cell yet all were connected into an electrical circuit. By taking the advantage of electro-physics rules governing the cells addition we managed to tune the operational voltage and the capacitance.

However, the cells strings to be ultimately attractive and viable for electronic applications must demonstrate the performance uniformity for the individual micro-EDLCs. One of the important aspect of this issue is the reproducibility and yield of the micro-EDLCs fabricated in a one process flow.

In this paper we report the comparison of co-fabricated on-chip circuits consist of monolithically integrated micro-EDLCs connected in parallel, in series, and individual cells in circuits about their patternability and electrochemical performance. Finally, we did a comparable study (section 3) and discussion (section 4) of obtained results. Based on the performance deviation among the micro-EDLC in a circuit we could estimate the major advantages and drawbacks of used technology. These important points represent some of the fundamental steps towards the on-chip large-scale integration of the IEDCs.

2. Integrated Energy Device Circuits

The 1-10 in series and in parallel samples were fabricated following the fabrication process described in [2].

2.1. CNT electrodes

The mesh electrodes consist of dense packed single wall Super Growth CNTs (SGCNT) forest grown by water assisted CVD process [3]. The SGCNT forest is characterized by high impurity and Specific Surface Area (SSA, > 1000 gcm\(^{-3}\)). To make the uniform and thick film, we developed the homogenous, high viscous, 0.5 wt.-% suspension of SGCNTs in 1-Methyl-2-pyrrolidinone (NMP). The paste was used for a paint-like coating on the substrate area with patterned electrical pads and cell barriers for an electrochemical isolation. Next, the coated paste was dried to get the CNT film free of a solvent. Finally, the micro-meter thick interdigitated electrodes were released.

3. Results

All of the electrochemical measurements were done using two electrodes set-up of VMP3 (Bio-logic Instruments, US). The thickness of the CNT electrodes was determined by a 2D surface profiler Dektak 150 (Veeco Instruments, US). The determination of \(iR\) drop, calculation of the capacitance were performed the same style as it was reported in [2].

3.1. 1-10 cells in series and in parallel

![Figure 1](image1.png)  **Figure 1.** Graph: no. of cells connected in series vs. av. current.

![Figure 2](image2.png)  **Figure 2.** Graph: no. of cells connected in parallel vs. av. current.
Previously we reported the strings of 1-10 cells in series and in parallel that trend lines of the operational voltage and capacitance satisfied the electro-physics rules governing cells addition [2].

From that point we assumed the uniformity of the cells is approved. However, this time we decided to take a detail look on the performance characterization. Figure 1 and 2 present the charged and discharged currents level for 1-10 cells in series and in parallel, respectively, obtained from cyclic voltammetries (CVs). The charge-discharge currents for particular connections showed mirror responses except for 10 cells in parallel connection. The current values for the anode and the cathode were -20.04 μA and +36.34 μA, respectively. In all cases the maximum divergence from the trend lines equals to +/-0.35 μA and +/-13.00 μA for in series and in parallel connections, respectively. The divergences could be a consequence of: 1) a non-uniform pore network, 2) various electrodes volume, 3) the leakage current reflected in an iR drop, 4) various equivalent series resistance (ESR), which include the contact resistance between CNT electrodes and metal electric pads, 5) the ohmic resistance of the electrical pads.

3.2. Individual cells combined in a string

In order to understand the origins of the divergence in the current responses, reported in section 3.1, we did measurements of individual micro-EDLCs being in a string. Not all of the 10 cells in a string were possible to measure; cell no. 2 and 3 have a short circuit between the CNT cathode and anode. Nonetheless, the other cells presented in figure 5, due to independent leads, were characterized.

First, we checked how much the CNT electrodes differentiate in a thickness obtained from a 2D surface profiler, Average Height Step (ASH, figure 3). We assumed the electrodes areas are invariant.

![Figure 3](image-url). Optical microscope photography: cells in a string (up); graph: distance vs thickness of electrode (down).

![Figure 4](image-url). Graph: comparison of CVs: voltage vs current conducted at 500 mV/s.

![Figure 5](image-url). Graph: comparison of CCCDs: time vs voltage conducted at 0.2 mA cm⁻³.

![Figure 6](image-url). Graph: comparison of impedance spectras: frequency vs impedance phase angle.
due to the photolithography technique we used for patterning. The electrode thickness of cell no.1 and 4 (~3.3 μm) attained about 60% of the thickness of the other six measured cells (4.5-6.4 μm, table 1). The thickness results was used to estimate the total volume of the CNT electrodes.

The surface roughness (Ra) of the electrodes are in the range of 390-905 nm (table 1). Further, from CVs (figure 4), CCCDs (figure 5) we got the various responses of the individual micro-EDLCs to deduce the capacitances and iR drops. Additional, we performed the Potential Electrochemical Impedance Spectroscopy (PEIS) at 0V with 10 mV amplitude in order to confirm the impedance angle response vs frequency, a time relaxation constant, τ (figure 6), and ESR (figure 7). All the data were summarized in table 1 to give a comparative summary of individual micro-EDLCs in a string.

### Table 1. Comparative summary of the performance of individual cells in a string.

| Cell no. | Electrode thickness, ASH (nm) | Ra (nm) | Electrode volume (x10^3 cm^3) | Capacitance based on CV (μF) | Capacitance based on CCCD (μF) | iR (V) | τ (s) | ESR (Ω) |
|----------|-----------------------------|--------|-------------------------------|-----------------------------|-------------------------------|--------|------|--------|
| 1st      | 3286.97                      | 679.48 | 1.57                          | 7.86                        | 7.24                          | 0.12   | 0.002 | 27     |
| 4th      | 3392.15                      | 389.71 | 1.62                          | 8.76                        | 8.01                          | 0.14   | 0.001 | 32     |
| 5th      | 5695.76                      | 582.19 | 2.71                          | 16.82                       | 16.39                         | 0.11   | 0.013 | 28     |
| 6th      | 6418.25                      | 780.64 | 3.06                          | 17.86                       | 16.98                         | 0.08   | 0.005 | 28     |
| 7th      | 5021.89                      | 561.97 | 2.39                          | 17.50                       | 17.50                         | 0.09   | 0.005 | 30     |
| 8th      | 5129.20                      | 502.22 | 2.44                          | 17.39                       | 16.98                         | 0.12   | 0.011 | 35     |
| 9th      | 5474.81                      | 720.52 | 2.61                          | 17.54                       | 20.12                         | 0.11   | 0.005 | N/A    |
| 10th     | 4516.61                      | 904.49 | 2.15                          | 8.76                        | 13.51                         | 0.11   | 0.002 | 27     |

4. Discussion

The purpose of the evaluation of monolithic integrated micro-EDLCs was to determine the factor that has the major influence on the cells uniformity. At this stage we would like to confirm the level of uniformity of our IEDC by comparative study of cells’ performances being monolithic connected in a string.

We found the discrepancy in capacities among micro-EDLCs being in the range of (7.24-20.12) μF from CCCD tests, and (7.86-17.86) μF from CVs (table 1). We relate it to the unstable CNT suspension used to form the mesh electrodes; within short time (hours) since the dispersion process had been finished, we observed the separation of the CNTs/solvent and the solvent. Moreover, the separation was present during the formation of the CNT film resulting in diversified CNTs distribution. Thus, the variation in the CNT film thickness hence electrodes volumes were unavoidable (figure 3 and table 1). The origins of the mechanism standing behind this issue is under the investigation. We suppose it might cause some local CNT agglomerations that disallow the isolation.
of polarized electrodes within one cell, as it happened in case of cells no.2 and 3 (short circuit) decreasing the yield of working cells.

Additional $iR$ drops (figure 5 and table 1) were estimated to be in range of (0.09-0.14) V. Here, $iR$ drop is assigned to the inner pore network of CNT mesh electrodes. For operational voltage equals to 1 V it is about 1% difference. From the impedance spectra graphs we could notice analogous energy dissipations for cells (figure 6) and line profiles related to diffusion impedance elements (figure 7). The $ESRs$ from the Nyquist Plots (figure 7 and table 1) were resembling (27-35) Ω what means the formation of contacts between the CNT mesh and metal pads had a similar structure. All of these results indicates the identical inner pore network among cells, though the recalled separation phenomena took place.

The impedance phase angle -90 deg was kept up to 0.2 Hz (figure 6) and is not applicable for the electronics applications. However, we believe by the modification of a pore size in the CNT film and an electrode thickness we could enhance the frequency response.

Towards the reproducible IEDCs, which possess reliable long life cycling, we need comparable electrodes in their volumes. One of the solution is to focus on obtaining the uniform thick film by improvement of the coating technique.

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