Carbon Nanotube Enhanced Ultracapacitor

Riccardo Signorelli, Joel Schindall, John Kassakian

Massachusetts Institute of Technology, Laboratory for Electromagnetic and Electronic Systems

Introduction Ultracapacitors or double layer capacitors (DLCs) are energy storage devices whose operation is based on the double layer effect [1]. By utilizing highly porous carbon material with a surface area up to 2000m^2/g as electrodes (as in Fig. 3) commercial DLCs can achieve a energy density (6Wh/kg) much greater than the energy density of a conventional capacitor. However, this figure is much lower than the energy density reached by Lithium-Ion batteries (120Wh/kg).

Project Goals Design and Implement an Ultracapacitor cell (see Figs. 1 and 3) based on **Carbon nanotubes (CNTs)** that can enhance the performance achievable by batteries. Our analysis shows that the utilization of a matrix of vertically aligned CNTs (see Fig. 2 - right) as electrode structure, can lead to an ultracapacitor characterized by a power density greater than 100kW/kg (three orders of magnitude higher than batteries), a lifetime longer than 300,000 cycles, and an energy density higher than 60Wh/kg.

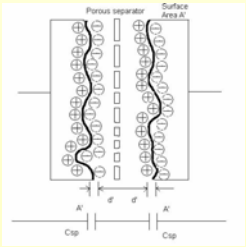

Fig. 1: Schematic of the components of a carbon based DLC.

Double Layer Principle The significant energy density improvement of DLCs over other types of capacitors arises from the higher specific capacitance achieved with DLCs that can be up to 180 F/g. This result can be explained by the double layer principle discovered by Helmholtz in 1853 [1]. According to the Helmholtz model, when two electrodes, between which a potential is established, are immersed in an ionic solution, ions from the electrolyte migrate to the interface between the oppositely charged electrode and the solution.

$$C_{SP} = \frac{A' \cdot \varepsilon_0 \cdot \varepsilon_R}{d'} \quad (1) \qquad U_{SP} = \frac{1}{2} C_{SP} \cdot V^2 \quad (2)$$

In the first order approximation, this enhancement in specific capacitance and energy density for a DLC are given by (1) and (2) where A' is the total surface area, and d' the distance between the double layer of charge in the solid electrode and in solution. Therefore, the high surface area presented by each electrode (A'), which can be up to 2000m^2/g, combined with the very small effective spacing between the two layers of charge (d') (ions in solution and electric charge in solid), which is smaller than 1 nm, leads to a high specific capacitance and, therefore energy density.

Carbon Nanotubes Carbon Nanotubes (CNTS) were first discovered by Iijima at the NEC laboratory in 1991 [2]. Fig. 2 (left) shows high resolution TEM micrographs of the concentric wall structure of the multi wall nanotubes (MWNTs) first observed by Iijima [2]. Single wall nanotubes (SWNTs) are composed of a single rolled up graphene layer to form a cylindrical wall one carbon atom thick.

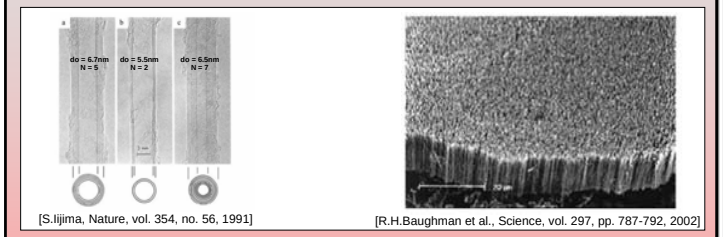

Fig. 2: (Left) TEM Micrographs of multi wall coaxial nanotubes with various inner and outer diameters, di and do, and numbers of cylindrical shells N reported by Iijima in 1991: (A) N = 5, do = 6.7nm; (B) N = 2, do = 5.5nm; and (C) N = 7, di = 2.3nm, do = 6.5nm. (Right) SEM micrograph of a film of vertically aligned CNTs with estimated density of 10^7tubes/mm^2.

Ballistic Conduction in Carbon Nanotubes The conduction phenomena in SWNTs and MWNTs with diameters smaller than 50nm is ballistic over lengths of several microns. Although for CNTs longer the few tens of microns the conduction is diffusive, the conductivity in CNTs hundreds of microns long is still more than two orders of magnitude higher than silicon. In an ultracapacitor this leads to reduced internal resistance and high power density.

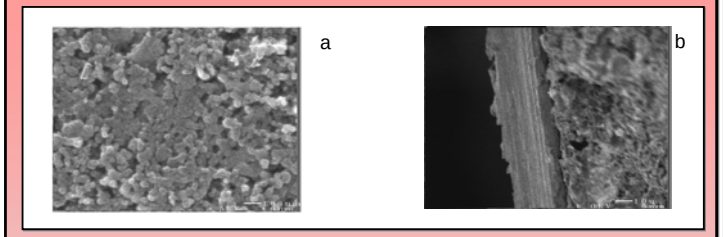

Fig. 3: (A) SEM micrograph of the top surface of an activated carbon based electrode. (B) SEM micrograph of the cross section of an activated carbon based electrode.

Nanotube Enhanced Ultracapacitor A matrix of vertically aligned carbon nanotube (CNT) has been investigated as a DLC electrode (see Fig. 2 right). Our analysis shows that this configuration can provide a combination of high power density (more than four orders of magnitude greater than fuel cells) and energy density (comparable to Li-Ion batteries). The significant enhancement in the achievable DLC power density derives from the high conductivity obtainable with CNTs, which in the limit of a few microns in length present ballistic conduction. The energy density improvement of a "nanotube enhanced electrode" is due to the higher effective surface area obtainable with a structure based on vertically aligned nanotubes over activated carbon (Fig. 3 a and b).

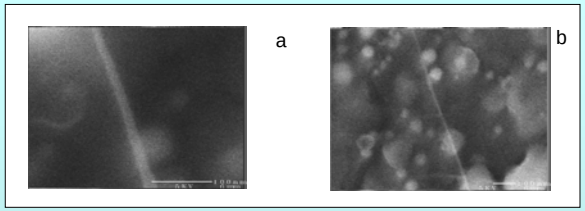

Fig. 4: (a) SEM micrograph magnifying the SWNT. (B) SEM micrograph of a SWNT surrounded by catalyst particle and impurities on the surface of the Si substrate.

CNT Growth Results Recently, we have been able to grow straight single wall nanotubes with diameters varying from 0.7 to 2nm and a length of several tens of microns. Figs. 4 a and b show SEM pictures of the as-grown SWNTs.

Fabrication We grew SWNTs via thermal chemical vapor deposition (CVD) (see Fig. 5 a) on a silicon substrate coated with a catalyst consisting of nanocolloids of aluminum oxide (AlO_2) coated with iron nitrogen oxide ($Fe(NO_3)_3$). The average diameter of the catalyst seeds was 3nm. The substrate coated with catalyst was processed at 900°C at atmospheric pressure by CVD in an environment saturated with hydrogen (H_2) and argon (Ar). As stockfeed gas we used methane (CH_4). Single wall nanotubes grew from the $Fe(NO_3)_3$ seeds (bottom growth process see Fig. 5 b) via decomposition of methane at the catalyst interface. Currently, we

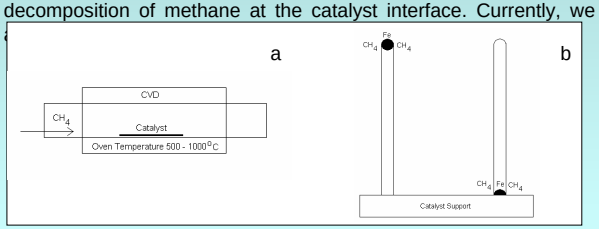

Fig. 5: (a) Illustrative view of a CVD furnace. (b) Schematic of bottom growth process (left) and top growth (right) of a single wall nanotube.

References

[1] H. von Helmholtz, Ann. Phys. (Leipzig), vol. 89, p. 211 (1853).
[2] S.Iijima, Nature, vol. 354, no. 56, (1991).
[3] K.H.An et al., Adv. Func. Mater., 11, pp. 3871-392, (2001).
[4] R.H.Baughman et al., Science, vol. 297, pp. 787-792, (2002).

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