Carbon Nanotube Enhanced Double Layer Capacitor

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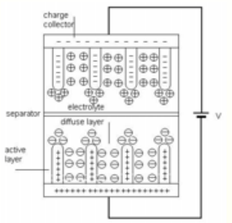
Introduction and Project Goals A double layer capacitor (DLC), often called an ultracapacitor, utilizes a activated carbon electrodes (Fig. 1) together with an ionic electrolyte. By means of the Helmholtz effect this structure exhibits a capacitance, hence an energy storage capability that is several orders of magnitude higher than a conventional electrolytic capacitor (Tab. 1). Our project focuses on the development of a carbon nanotube based ultracapacitor also called nanotube enhanced ultracapacitor (NEU). Our NEU can potentially achieve energy densities between 30 and 80 Wh/kg, which is comparable to electrochemical batteries.

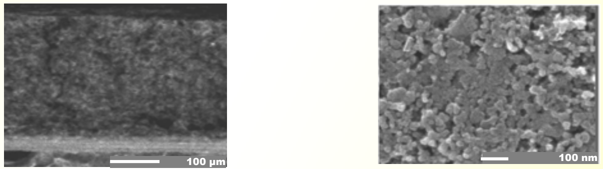
	DLC (typical)	Li-Ion (typical)	MIT NEU Expected Performance
Energy density (Wh/kg)	5.44	140	30 - 80
Power density (kW/kg)	5.61	0.2	40
Rated voltage (V)	2.7	2.2	3.5 - 4
Longevity (cycles)	300,000	300-1000	300,000
Robustness and reliability	Excellent	Good	Excellent
Temperature dependency	Minimal	Moderate to high	Minimal



Tab. 1: Performance comparison among commercial lithium-ion batteries, commercial activated carbon based ultracapacitors and the MIT nanotube enhanced Ultracapacitor.

Fig. 1: Schematic representation of the nanotube enhanced ultracapacitor electrode structure.

The expected power density of the "nanotube enhanced ultracapacitor" (NEU) is greater than 40 kW/kg, which significantly exceeds that of lithium-ion batteries and is comparable to that of electrolytic capacitors. In addition, the rated voltage of our device is expected to be greater than 3.5 V.



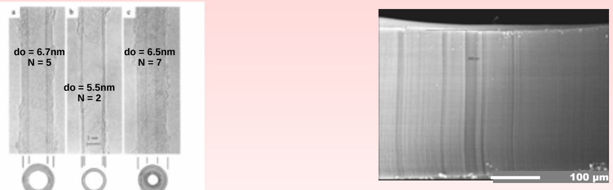
[R.Signorelli – January 2004]

[R.Signorelli – January 2004]

Fig. 2: (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.

Double Layer Principle The energy density improvement of DLCs over other types of capacitors arises from the specific capacitance achieved with DLCs that can be up to 180 F/g for commercial devices. This result can be explained by the double layer effect discovered by Helmholtz in 1853 [1]. According to his model, when two electrodes, between which a potential is established, are immersed in an ionic solution, ions from the electrolyte migrate to the charged electrode forming the double layer of charge with it. In the first order approximation, the DLC enhancement in specific capacitance is given by the surface area of the double layer of charge (electrode/electrolyte), as high as 2000 m^2/g, and by the distance between the two layer of charge, as small as 1 nm.

Nanotube Enhanced Ultracapacitor The graphite like structure of carbon Nanotubes (CNTS) was first observed and described 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) 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.

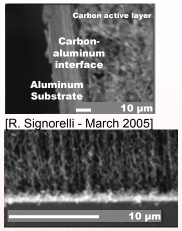


[S.Iijima, Nature, vol. 354, no. 56, 1991]

[R.Signorelli – July 2005]

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 Ilijima 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 cross sectional micrograph of a film of vertically aligned CNTs

Our analysis shows that a matrix of vertically aligned carbon nanotube (CNT) as a DLC electrode (see Fig. 2 right). can provide a combination of high power density (more than four orders of magnitude greater than batteries) and energy density (comparable to Li-Ion batteries) (Tab. 1). The significant enhancement in the achievable DLC power density derives from the high conductivity obtainable with CNTs. The energy density improvement over activated carbon of a "nanotube enhanced electrode" is due to the electrochemical properties of CNTs and by the features of the vertically aligned nanotubes.



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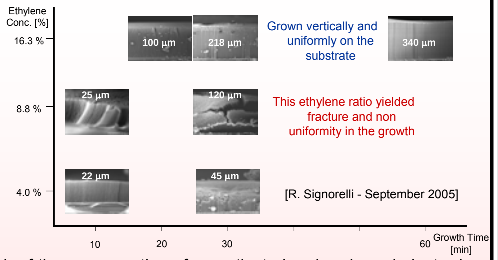


Grown vertically and uniformly on the substrate

This ethylene ratio yielded fracture and non uniformity in the growth

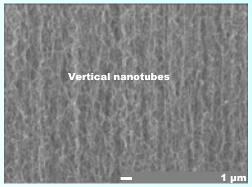
[R. Signorelli - September 2005]

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

Graph 1: Dependence of the nanotube length over the ethylene concentration and the growth time.

Electrode Fabrication The active layer of the DLC electrodes based on the vertical nanotube forest are fabricated via chemical vapor deposition (CVD) of ethylene. A conducting Si substrate coated with a thin film of alumina and iron acting as a catalyst are introduced in the CVD chamber giving raise to the self assembly of the vertical nanotube film. The growth rate and the length of the nanotubes can be controlled by the ethylene concentration in the forming mixture and by the growth time as shown by Graph 1. Conversely than activated carbon electrode, our process allow to grow the active layer of nanotube directly on top of the charge collector (Fig. 3). This constitute a significant improvement in the electrode resistance and DLC power density.

[R.Signorelli – August 2005]



	Target	*Current*	*Comment*
Vertically aligned CNTs			Achieved
High tube density:		On target range	Under investigation
Tube spacing:	Optimized depending on electrolyte	Fixed spacing	Under investigation
Tube diameter:	SWNTs	Small MWNTs	Under investigation
Tubes length:	150 - 500 µm	350 µm	Achieved
Suitable DLC substrate material	Suitable for CNT growth DLC friendly	Conducting Suitable for CNT growth	Partially achieved
Charge Collector Thickness	10 µm		To be started

Fig. 4: SEM micrograph magnifying the structure of vertically aligned nanotubes.

Tab. 2: Presentation of the state of the electrode fabrication compared to the goal of the project.

Current State of the Research As Tab. 2 summarizes we have currently achieved the growth of vertically standing CNTs and we are currently working on the optimization of the CNT spacing and diameter (see Fig. 4 shows for a magnification of the CNT film structure). Control over these features is necessary to better utilize different electrolytes. In addition, we are currently improving the ablity to grow vertical CNTs on fully conducting substrates. Lastly at this point we have achieved the ability to control the desired length of the CNT active film.

Nanotube Growth System Fig. 5 shows different parts of our low pressure chemical vapor deposition laboratory for the fabrication of our nanotube electrodes. Currently, we are upgrading the apparatus adding the capability of analyzing the grow gas mixture used.

Fig. 5: Illustration of the vertically aligned nanotube chemical vapor deposition growth plant. (a) Gas mixture control cabinet. (b) Vacuum seal and pressure gauge. (c) Panoramic view of part of the plant.

References

[1] H. von Helmholtz, Ann. Phys. (Leipzig), vol. 89, p. 211 (1853).
[2] S.Iijima, Nature, vol. 354, no. 56, (1991).

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