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Electrochemical Double-Layer Capacitors Using Carbon Nanotube Electrode Structures

These capacitors can store large amounts of energy and deliver very high peak power; they are used in electric vehicles and may have applications in linear motor drives.

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ABSTRACT | The structure and behavior of the electrical double-layer capacitor (EDLC) are described. The use of activated carbon electrodes is discussed and the limitations on voltage and accessible surface area are presented. Metrics for evaluating EDLC performance are defined and previously reported results of experimental carbon nanotube (CNT) electrodes are tabulated. New experimental results of electrodes constructed of vertically aligned CNTs grown on a conducting substrate are presented. By extrapolating prior and new experimental data the energy density of CNT-based EDLCs is shown to be potentially up to seven times that of commercial activated carbon-based EDLCs.

KEYWORDS | Double-layer capacitors; capacitors; carbon nanotubes; energy storage; ultracapacitors

I. INTRODUCTION

The electrochemical double-layer capacitor (EDLC), also known as an ultracapacitor or supercapacitor, exploits the double-layer of charge formed when a voltage is applied to an electrode immersed in an electrolyte. Further, the electrodes of an EDLC are constructed of highly porous carbon resulting in a very large surface area to volume ratio. Fig. 1 shows schematically the construction of an EDLC comprising two carbon electrodes, each with a double-layer of charge at the electrolyte interface. The very small charge separation in the double-layer and the large surface area of the electrode results in a specific capacitance on the order of 40–60 F/cm^3. The breakdown field strength of the EDLC, calculated in V/cm, is extremely high relative to that for conventional capacitors. These three factors—high surface area, small charge separation and high field strength—give rise to the very high energy density achievable with the EDLC. The EDLC, first described by Rightmire in 1966 [1], should not be confused with the electrolytic capacitor which is comprised of two metal foil electrodes (typically Al or Ta), one of which has an oxidized surface, separated by electrolyte soaked paper and rolled into a tubular form. The oxide layer forms the dielectric, its thinness and high breakdown voltage giving rise to the high specific capacitance of electrolytics relative to solid film capacitors. An EDLC has a volumetric capacitance on the order of $10^6 - 10^8$, that of an electrolytic of comparable physical size. However, since the working voltage of the EDLC is about 10^{-2}, that of an electrolytic, the energy density of commercial EDLCs is about $10^2 - 10^3$, that of electrolytics. On the other hand, the low ESR of the EDLC produces a device with an extremely high power density.

As the energy density of EDLCs has increased they are being viewed as a potential replacement for batteries. With their much longer cycle life and better behavior as a function of temperature they are an attractive alternative. A parametric comparison between EDLCs and Li-ion batteries is shown in Table 1.

The carbon forming the electrodes of the EDLC, made highly porous by a thermal activation process yielding activated carbon (AC), is attached to the metallic current
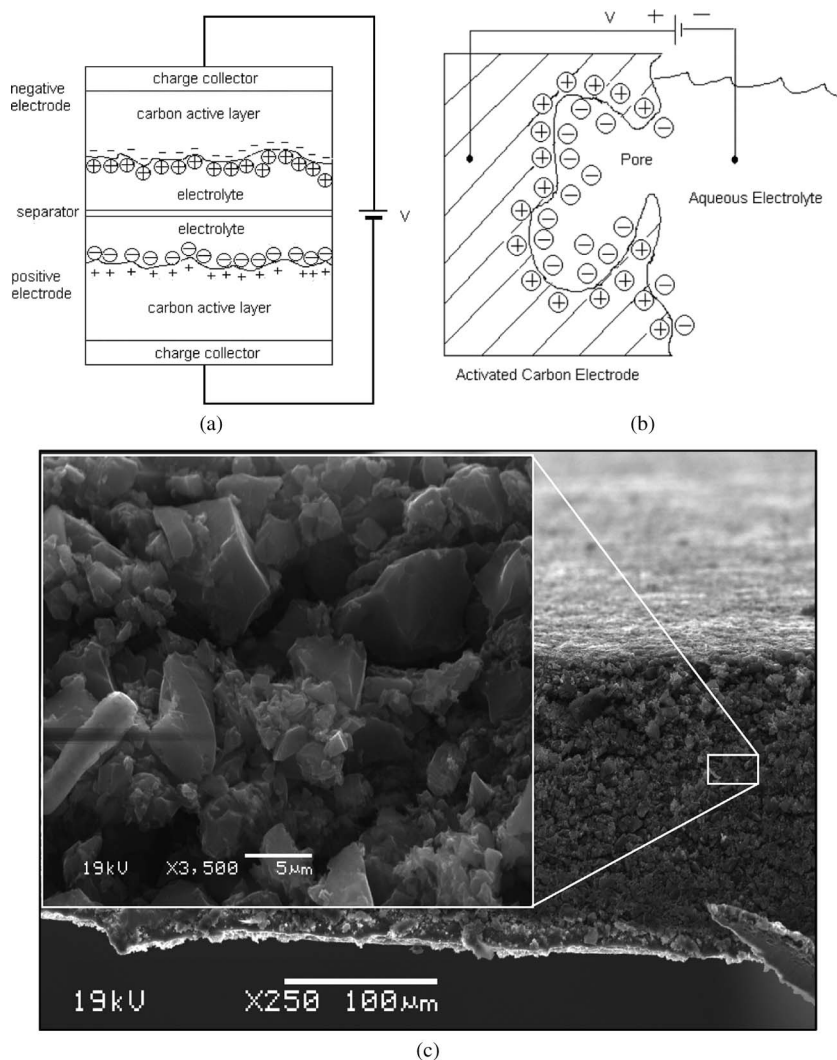
Fig. 1. *(a) Schematic of an activated carbon-based EDLC. (b) Representation of pore in carbon electrode active layer. (c) Electron micrograph of activated carbon electrode.*

collector using a bonding agent. The working voltage of the device is limited by the stability of the electrolyte and is typically on the order of 2–3 V. This low voltage is partly due to electrolyte contamination caused by both the carbon activation process and the bonding agent.

Table 1 Parametric Comparison Between a Commercial Activated-Carbon Based EDLC and a Li-Ion Battery [6]

Attribute	Li-ion battery	EDLC
Power density (kW/L)	3	10
Energy density (Wh/kg)	100	5
Rate capability X (XC)	<40	>1800
Minimum T (^{o}C)	0	-40
Maximum T (^{o}C)	+40	+65
State-of-charge excursion (%)	50	100

The EDLC is being applied with increasing frequency to systems demanding high peak power for short durations. One such application is in hybrid vehicles where regenerative braking, acceleration and electric power steering all have power requirements fitting this profile. Nissan [2], Honda [3], and Toyota [4] have all employed EDLCs to supplement the battery in hybrid vehicles, and the use of EDLCs to provide satisfactory transient behavior of experimental fuel cell vehicles has been described [5].

One of the distinguishing characteristics of EDLCs is the multiple time constants exhibited by their charging and discharging behavior. Fig. 2(a), showing voltage as a function of time under constant current charging, is illustrative of the dependence of the incremental capacitance on the state of charge. Fig. 2(b) illustrates a simple model for a commercial 2500 F EDLC with the experimentally determined parameter values. The lumped time constants represent the varying degree of difficulty of ions penetrating
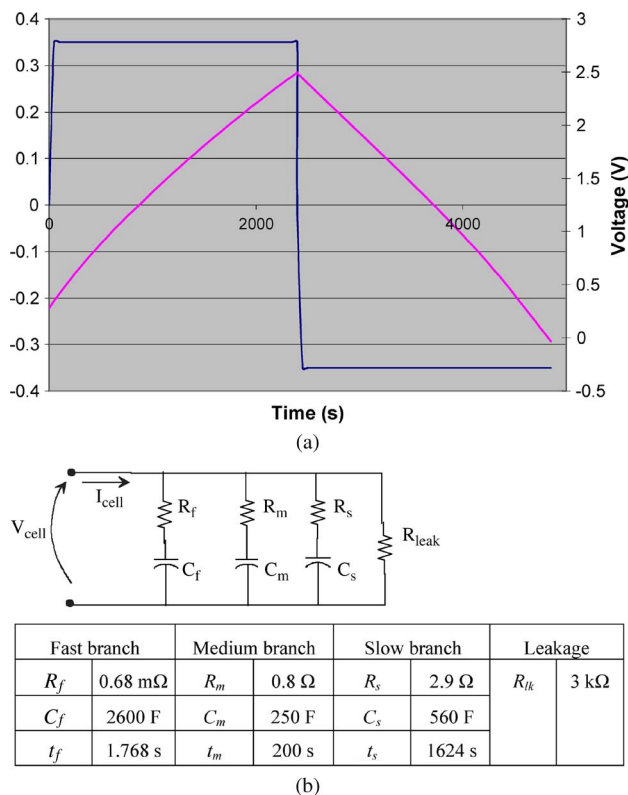
Fig. 2. (a) Constant current charge profile for a 350 F activated carbon-based EDLC. (b) Simple equivalent circuit of a 2500 F EDLC illustrating the multiple time-constant nature of its behavior [7].

the various pore sizes in the activated carbon electrode. That is, the transport of ions into long narrow pores is slower than that of ions into wide shallow pores.

II. EDLC METRICS

The basic measures of EDLC performance are the electrode surface area, the electrode area-specific differential capacitance, the electrode volumetric capacitance, the frequency behavior of the impedance, the shape of the cyclic voltammetry trajectory, and the ESR which is reflected in the power density of the device.

The electrode surface area—the total nonplanar surface area of the carbon—is measured using a technique known as the BET method, and the result is known as the BET surface area with units of m^2/g. The method is named for Braunauer, Emmett, and Teller, who in 1938 described analytically the adsorption of gas on a solid surface [8]. The measurement is made by relating the weight of a monolayer of gas adsorbed on the accessible surface of the carbon electrode to the surface area of a uniform monolayer of the gas.

The electrode area-specific capacitance in units of F/cm^2, commonly known as the differential capacitance or intrinsic capacitance, C_D, is the incremental capacitance

(dQ/dV) of 1 cm^2 of the BET measured surface area of the carbon. It is a function of both the measurement frequency and bias voltage. The frequency dependence arises because of the different transit times of ions penetrating the different pore sizes in the carbon. The voltage dependence is due to the nonlinear relationship between the charge in the Helmholtz layer and the potential between the solid electrode and the bulk of the electrolyte, and for low electrolyte molarities is most pronounced at a potential far from the potential of zero charge. For high electrolyte molarities, at higher voltages, the incrementation of surface charge by the presence of a charge diffusion layer causes the measured C_D to become approximately constant with voltage.

The gravimetric capacitance of the carbon electrode is an often cited metric. Assuming that the entire BET surface area is accessible to the ionic charge, the gravimetric specific capacitance can be approximately calculated by the product of C_D and the BET surface area. However, as with C_D, it does not provide a measure from which the performance of an EDLC could be inferred, since these metrics do not reflect electrode planar surface area.

The volumetric specific capacitance, however, provides a useful comparative measure of EDLC electrode performance. It is the capacitance of 1 cm^3 of electrode volume. Because it reflects the density of pores, or how tightly packed a nanotube structure is, as well as the area specific capacitance, it allows a relative measure of the physical size of a device with a specific rating.

Impedance data is generally presented as the traditional Nyquist diagram of the small-signal impedance around a bias. Fig. 3 shows a diagram typical of an EDLC. The nearly vertical behavior at frequencies below 0.6 Hz represents behavior dominated by capacitance. We refer to this breakpoint (0.6 Hz) as the "knee" frequency. The behavior between 0.6 Hz and 200 Hz, characterized by a 45° locus,
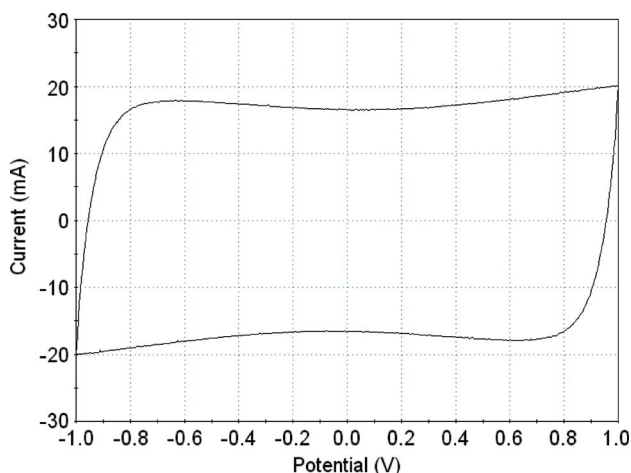

Fig. 3. Voltammetry diagram for an EDLC cell with 1 cm^2 activated carbon electrodes.
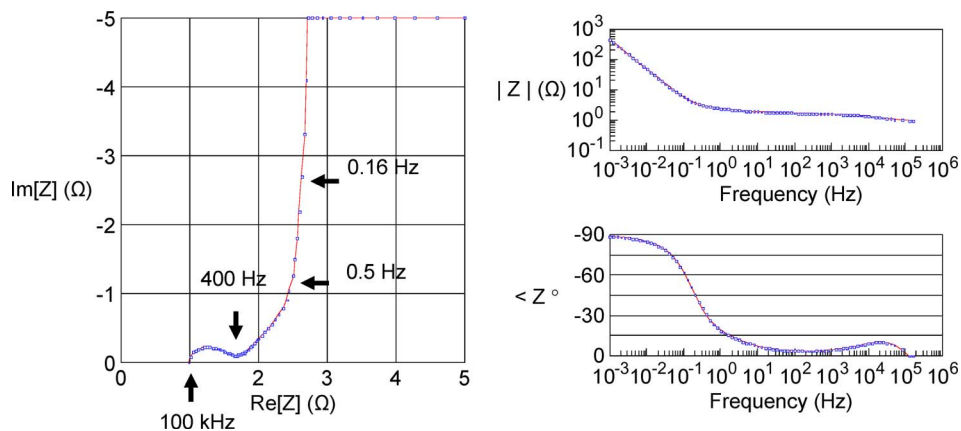
Fig. 4. *Nyquist and Bode plots for a 1 cm^2 EDLC cell with two 135 mm thick activated carbon electrodes.*

represents an impedance influenced by the diffusion of charge into pores and reflects the transmission line-like model of Fig. 2.

Cyclic voltammetry is an electrochemical analysis technique that plots the electrochemical cell current against its voltage at a fixed magnitude of rate of change of voltage (the scan rate). The waveform of the scan voltage vs. time is triangular. The technique is most often used in the investigation of Faradaic reactions, that is, reactions that involve mass transfer. In theory an EDLC does not involve a Faradaic reaction. In practice, however, there are Faradaic components to the EDLC behavior and cyclic voltammetry can provide insight to these processes. A pure capacitor of constant capacitance has a rectangular cyclic voltammetry plot. A nonzero ESR will create exponential transitions to a constant current at the voltage where the scan changes sign. A noninfinite shunt resistance will create an increasing current with increasing voltage, i.e., the plot will become trapezoidal. At voltages high enough to initiate a redox reaction the current increases in an exponential fashion. The shape of the voltammetry plot manifests the complexity of the electrochemical processes at play in the EDLC. Fig. 3 shows the voltammetry diagram for a EDLC cell comprising 1 cm^2 activated carbon electrodes.

The ESR of an EDLC cell is a function of frequency, as illustrated by the Nyquist diagram of Fig. 4. At very low frequencies, the ESR is fairly constant, but at frequencies above the knee the ESR decreases, which is consistent with the frequency behavior of the model of Fig. 2. The power density of an EDLC is determined from the *IR* drop seen at the terminals when a step of current is applied. The power is then calculated for a load matched to this resistance. When in the context of experimental electrode materials, this parameter is generally expressed as the gravimetric power density kW/kg of electrode material, e.g., the weight of the activated carbon or carbon nanotubes. As a practical matter, the power density provides a comparative measure of the pulsed power capability of EDLCs.

While commercial devices are characterized by specific capacitance, energy density and power density normalized by packaged weight and size, experimental results of carbon nanotube based electrode research are not presented in a canonical form. Presented results can be normalized by current collector (planar electrode) surface area, electrode (total nanotube) surface area, carbon weight, carbon plus current collector weight, carbon plus current collector plus separator plus electrode weight or volume, etc. Experiments are done using small electrode samples (e.g., 1 cm^2) tested in various electrolytes using custom designed test cells. An EDLC is composed of two electrodes with a porous separator between them. Each electrode represents a double-layer capacitor of value C. The packaged EDLC thus has a capacitance C/2. When interpreting experimental data presented in the literature it is necessary to know whether the data is for a single electrode or a two electrode cell. Thus one must be careful in making performance comparisons among different published results. In what follows we have either normalized published results to a common reference where possible, or indicated the measurement conditions. The power density (kW/kg) is frequently specified for experimental electrodes. This parameter is meaningless in early experimental results as it is a function of only the voltage and ESR. The ESR in experimental cells is not indicative of the ESR of a properly packaged device with practical electrodes. Thus we focus on the volumetric and gravimetric energy densities.

III. CURRENT AREAS OF RESEARCH

There has been a considerable amount of effort in studying the growth of CNTs for a variety of applications. Through these efforts, growth of vertically aligned CNTs on silicon (Si) substrates with a transition metal catalyst of either nickel (Ni), cobalt (Co), or iron (Fe) has been well documented [9]. Aluminum oxide or alumina (Al$_2$O$_3$) is commonly used as the supporting substrate, which serves to

prevent the catalyst and substrate from interacting and allows for the proper catalytic nanoparticles to form. However, such combinations of materials are not suitable for use as electrodes due to their poor conductivity and their correspondingly high resistances. The principal issues confronting CNT-based EDLC research are achieving growth on a conducting current collector (substrate), density of tubes (i.e., tube spacing), carbon weight per cm^2 of collector (a reflection of density, length and number of walls), and achievable electrolyte molarity. At the present state-of-the-art, issues of packaging, manufacturability and cost are secondary, if not tertiary, considerations.

Niu *et al.* first introduced the idea of a DLC using entangled multiwalled nanotubes (MWNTs), achieving an energy density of 0.56 Wh/kg, based on the weight of the electrolyte, separator, and the two electrodes [10]. From the electrode density and volume of Niu's electrode one can compute the electrode only energy densities (volumetric and gravimetric) to be 3.1 Wh/l and 3.9 Wh/kg, respectively, for two electrodes. The Niu device utilized catalytically grown CNTs with an average diameter of 5.5 nm that were commercially produced by Hyperion Catalysis International. The CNTs were first pretreated with nitric acid to disassemble the as-produced nanotube aggregates. The individualized CNTs were then filtered, dried, and annealed to form an electrode of randomly entangled and thermally cross-linked CNTs. The CNT electrode had a uniform thickness of ~25.4 μm and required no binder since the functionalized carbon nanotubes are self-adhesive. Through the treatment the BET surface area increased from 250 to 430 m^2/g. Using 38 wt. % H$_2$SO$_4$ in water as the electrolyte, the maximum specific capacitance was 113 F/g or 90 F/cm^3 and the differential capacitance was 24 F/cm^2.

An *et al.* showed the specific capacitance achievable using an electrode based on heat treated single wall nanotubes (SWNTs) as the active layer [11]. The SWNT electrode consisted of 70 wt. % of randomly entangled and cross-linked SWNTs and 30 wt. % polyvinylidene chloride (PVDC) as the binder. The ratio of CNTs to binder was determined empirically. The electrode was then heat-treated for 30 minutes in argon at 900–1000 °C. After the heat treatment the electrode differential capacitance was approximately 50 μF/cm^2 and the BET surface area was 357 m^2/g. An's electrode achieved specific capacitances of 180 F/g and 135 F/cc in 7.5 molar KOH. The maximum energy density claimed by An is 6.5 Wh/kg (An's report does not specify whether these figures are relative to the electrode weight alone, or to the combined electrode, electrolyte, and separator weight). It was found that with increasing treatment temperature, there is a corresponding increase in specific surface area, a decrease in average pore diameter, and an increase in specific capacitance. Although the BET surface area is less than the 430 m^2/g reported in Niu's MWNT device, improvements in specific capacitance were attributed to the higher differential capacitance resulting from An's process.

The formerly discussed techniques were limited in their energy and power densities by either the need for pretreatment (Niu) or a binder (An), which increased parasitic resistances. The use of randomly entangled CNTs instead of vertically aligned CNT arrays also limits performance. Yoon *et al.* was able to decrease contact resistance by directly growing vertically aligned CNTs on an Ni foil metal collector [12]. No catalyst was deposited on the current collector. MWNTs were grown using the plasma-enhanced CVD (PECVD) method with methane and hydrogen as the reactant gases. The CNTs were then treated with an NH$_3$ plasma to remove carbon impurities introduced in the growth process. The measured dc capacitance of the NH$_3$ treated device was 207 F/g with a surface area of 86.5 m^2/g, yielding a reported differential capacitance of 240 F/cm^2. The directly grown CNT electrodes also exhibited rectangular cyclic voltammagrams at scan rates up to 1000 mV/s. However, the grown CNT array achieved a thickness of only 20 nm, which is insufficient for viable energy storage purposes.

The difficulty of growing a sufficient CNT array on a conducting substrate has resulted in a number of different techniques for implanting previously grown CNTs onto a metal current collector. Du and Pan fabricated CNT electrodes by electrophoretic deposition (EPD) [13]. CNTs grown from another source are first suspended in a solution of nitric acid. After filtration by distilled water and rinsing with ethanol, the CNTs are then dried. The CNTs are dispersed in ethanol by sonication and deposited on Ni foil under the influence of an electric field. This process is similar to the method of Niu *et al.*, except for the introduction of a metal current collector. The electrical resistance of the as-deposited EPD films is extremely high ($\sim$kΩ); however, after annealing in a hydrogen environment, there is a large decrease in the resistance. This may be attributed to electrochemical oxidation that takes place during EPD, which is then reduced through hydrogen treatment. Du and Pan report near-ideal rectangular cyclic voltammagrams at scan rates up to 1000 mV/s. The calculated specific capacitance is 84 F/g.

Kumar *et al.* have proposed a method of contact transfer of CNTs using low temperature solder alloys [14]. The process involves annealing a solder coated conducting substrate and placing it in close contact with a CNT array grown on a Si substrate. The CNTs then penetrate the solder surface and are entrapped and transferred after solidification of the solder. The use of solder provides a low contact resistance between the CNTs and the current collector. This method is capable of directly transferring an array of vertically aligned CNTs. A DLC produced using this procedure has not yet been reported. While transfer techniques sidestep the need to directly grow CNTs on a conducting substrate, producing DLCs using these methods require significant extra manufacturing steps as well as the need for a supply of CNTs from another source.

Recently, Futaba *et al.* have produced an *SWNT solid*— a highly dense, vertically aligned CNT structure [15].

It uses the surface tension of liquids to zip together a CNT forest initially grown on silicon. The zipping together of the CNTs demonstrates the potential for greater density in the growth of CNTs to produce a greater surface area. The "SWNT solid" has a density on the order of 8.3×10^{12} CNTs/cm^2, CNT diameters of 2.8 nm, and a BET surface area of 1000 m^2/g. An electrochemical cell was produced by sandwiching the SWNT solid between platinum sheets, using 1 M tetraethylammonium tetrafluoroborate (Et$_4$NBF$_4$)/propylene carbonate (PC) electrolyte. From the reported data the gravimetric and volumetric specific capacitances of Futaba's electrode can be estimated to be 60 F/g and 12 F/cm^3 (at very low current densities). The reported energy densities for a two electrode cell at 2.5 V are 13 Wh/kg and 10.4 Wh/l. The main limitation of Futaba's electrode is its poor differential capacitance of 6 μF/cm^2 when compared to that achieved by Niu (24 μF/cm^2) and An (50 μF/cm^2) with their electrodes. It may be that ions cannot freely penetrate the interstitial spaces of such a dense structure, i.e., much of the BET surface area does not participate in charge storage.

IV. CNT GROWTH ON CONDUCTING SUBSTRATES

We have fabricated multiwall carbon nanotubes (MWNT) on a variety of substrates using low-pressure chemical vapor deposition (LPCVD). The process uses a gas mixture of acetylene, argon, and hydrogen, and an iron catalyst deposited on the substrate using electron beam vaporization. Fabricated electrodes are 1 cm^2 and are tested in an experimental cell using 1.4 M acetonitrile. The purposes of these experiments has been to demonstrate the growth of long CNTs on a conducting substrate, determine the wetting properties of the electrolyte, identify process param-
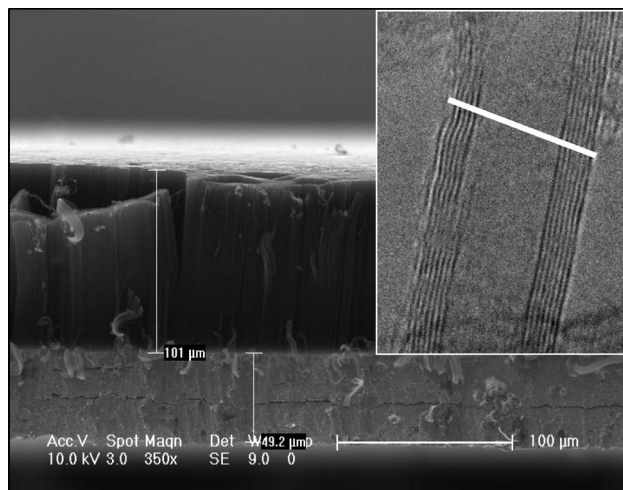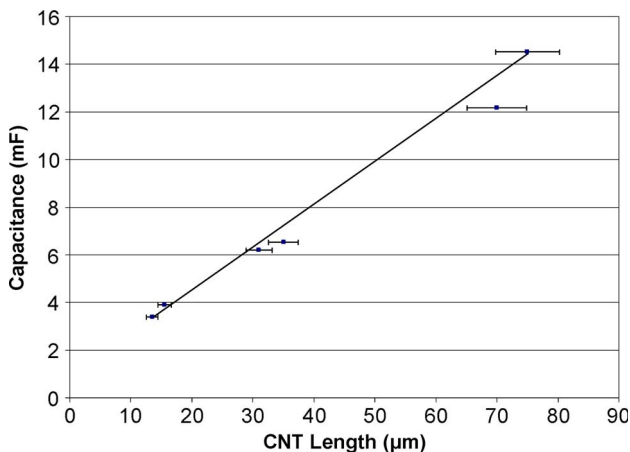

Fig. 6. *Measured capacitance vs. CNT length showing uniform wetting.*

eters that control CNT density and wall numbers, and provide measurements indicative of the electrical properties of the electrodes if applied to EDLCs.

Fig. 5 is an electron micrograph of CNTs grown on a tungsten substrate. The inset show a single seven-wall nanotube. On average, the as-grown CNTs have three walls and have been grown as long as 300 μm. Fig. 6 is a plot of the experimentally measured electrode capacitance as a function of nanotube length. The approximately linear relationship supports the assumption that the electrolyte is completely wetting the carbon layer. A caveat with respect to this conclusion is that the density of nanotubes in the samples on which these measurements were made was 5×10^{10}/cm^2, which is relatively sparse. It is yet to be shown that complete wetting occurs with higher tube densities, where the closer spacing of the nanotubes presents a greater wetting challenge.

The density of nanotubes was determined by removing the carbon layer and observing the residual tube "footprints" on the substrate surface. Using either AFM or SEM microscopy, the footprints were counted within a measured surface area. Fig. 7 is one such photograph showing the footprints as tiny circular divots. The maximum measured density achieved to date is 4×10^{11}/cm^2.

Knowing the density, average number of walls, diameter, and length of the tubes, and the density of carbon, the weight of the nanotube layer can be computed. Confirmation was obtained by weighing the electrode before and after nanotube growth. The resulting differential (carbon area specific) capacitance, C_D, was determined to be 10 μF/cm^2. This relatively low value is due to the lack of either thermal or acid aftertreatment of the nanotubes. The Nyquist and Bode plots for one electrode are shown in Fig. 8. These plots show a capacitance of about 16 mF for the 1 cm^2 sample, implying a two electrode cell capacitance of 8 mF.

In addition to tungsten, we have grown 100-μm-long CNTs on aluminum foil. Adequate adhesion was observed
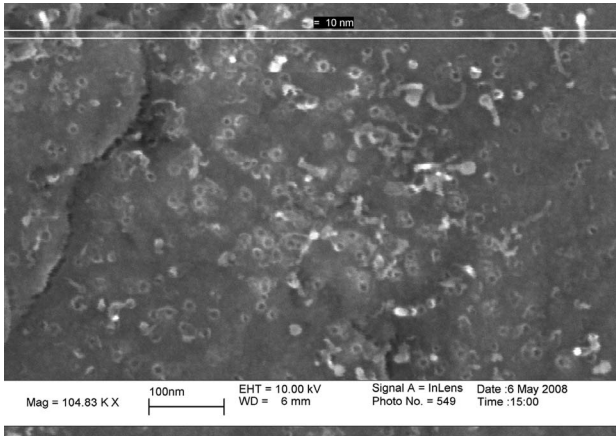

Fig. 5. *CNTs grown on a tungsten substrate with an aluminum interlayer. The inset shows a single nanotube having seven walls.*

Fig. 7. *Scanning electron micrograph of substrate after nanotube removal, showing "footprints" of the tubes as 6-nm divots.*

on ordinary kitchen foil prepared with a simple acetone cleaning. The good conductivity achieved suggests that the thin oxide layer always present on the aluminum is reduced at the iron catalyst sites.

V. ANALYSIS AND PERFORMANCE PROJECTION

We believe that the energy density currently achievable with commercial ultracapacitors can be enhanced using an electrode structure based on vertically aligned carbon nanotubes (VCNT) as the active layer. We base our calculations on reasonable extrapolations of the experimental results obtained by us as well as those reported by others as described previously. The model presented here shows that energy densities up to 21 Wh/kg and 22 Wh/l are obtainable at a voltage of 2.7 V for a packaged DLC cell using the VCNT-based electrodes that we propose. These values are

approximately four times those obtained today by the commercial activated carbon-based DLCs that are summarized in Table 1. In the event that a higher molarity electrolyte is practical, the CNT-based DLC can function up to 3.5 V, providing energy densities up to 35 Wh/kg and 37 Wh/l.

The morphology of the nanotube film we are attempting to fabricate is composed of nanotubes having an average diameter of 6.5 nm and three walls for each nanotube with an average spacing between nanotube centers of 10 nm, which corresponds to a nanotube density of $10^{12}/cm^2$. The length of the nanotube active layer is 200 μm. A 15-μm-thick aluminum film will be used as the charge collector (having a density ρ_{Al} of 2.7 g/cc). The accessible surface area of a triple wall nanotube is assumed to be 450 m^2/g, which is one–fourth that of a single wall nanotube, and its differential capacitance is assumed to be 50 μF/cm^2 (after proper treatment), which has been achieved by An [11]. The targeted operating voltage for the proposed cell (V_M) is 2.7 V. Although the absence of a contaminating binder and activation process would permit an operating voltage of 3.5 V, the high electrolyte molarity required to support this voltage will have other consequences that we have not explored. Therefore, 2.7 V and a molarity of 2.0 are assumed.

The electrolyte is assumed to be TEMA BF_4 in acetonitrile, which has a density of 0.8 g/cm^3. Common DLC separator paper is usable with our DLC cell. Its thickness is 10 μm, its density is 0.8 g/cm^3, and its porosity is 60% voids over the total paper volume. Table 3 lists the values of the electrode and DLC cell parameters upon which our energy density modeling and calculations are based.

VI. ELECTRODE AND CELL ENERGETIC COMPUTATIONS

The gravimetric (C_W) and volumetric (C_V) specific capacitances of a single VCNT electrode active layer can be
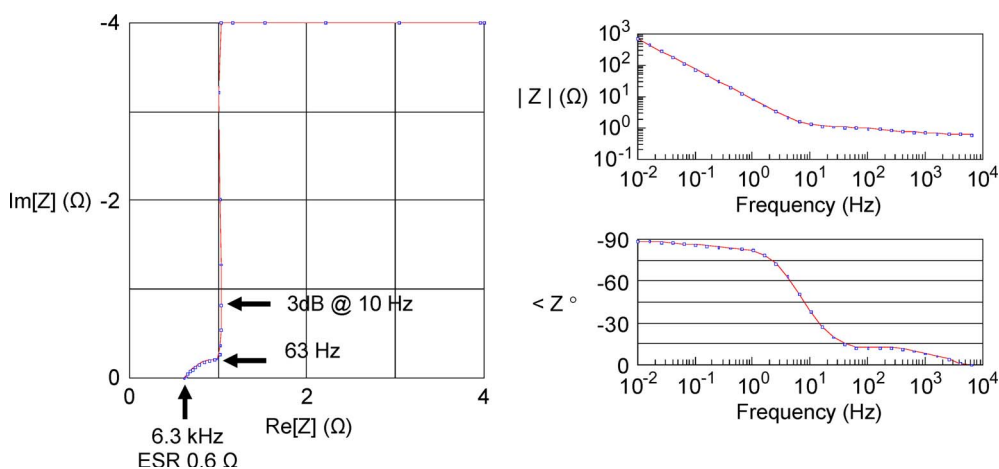

Fig. 8. *Nyquist and Bode plots for an EDLC cell using 1 cm^2 carbon nanotube electrodes. Measurements made at 0 V bias (1 M electrolyte).*

Table 2 Reported Experimental CNT Electrode Parameters

	V_M V	E_V Wh/l	E_G Wh/kg	C_G F/g	C_V F/cc	S_{BET} untreated m^2/g	S_{BET} treated m^2/g	ESR Ω	C_D uF/cm^2
Niu	1.0	3.1	3.9	113	90	250	430	0.094	24.0
Futaba	2.5	10.4	13.0	60	48	1000		0.039	6.0
An	0.9	3.8	6.5	180	135		357		50.4
Du	1.0		2.9	84					
Yoon	0.9		5.8	207			86.52		240.0

E_V : Volumetric energy density of a two electrode cell
E_G : Gravimetric energy density of a two electrode cell
C_V : Volumetric specific single electrode capacitance at dc
C_D : Specific differential single electrode capacitance
C_G : Gravimetric specific capacitance

calculated from the CNT active layer differential capacitance, surface area, and density

$$C_W = C_D \cdot A_3$$
$$= (50 \ \mu\text{F/cm}^2) \cdot (450 \ \text{m}^2/\text{g}) \cdot (10^4 \ \text{cm}^2/\text{m}^2)$$
$$= 225 \ \text{F/g} \tag{1}$$
$$C_V = C_D \cdot A_3 \cdot \rho_C = 102 \ \text{F/cm}^3. \tag{2}$$

The energy density of two VCNT electrode active layers in a DLC cell configuration is calculated under the assumption that the specific capacitances are constant with respect to voltage. This assumption leads to conservative estimates

since the DLC capacitance typically exhibits a slight increase with voltage

$$E_W = \frac{1}{8} C_W \cdot V_M^2 \cdot \frac{1}{3.6} = 57 \ \text{Wh/kg} \tag{3}$$
$$E_V = \frac{1}{8} C_V \cdot V_M^2 \cdot \frac{1}{3.6} = 26 \ \text{Wh/l}. \tag{4}$$

These energy densities are nearly double those reported by Niu, An, and Futaba as summarized in Table 2. The improvement is due to the assumption of an organic electrolyte allowing for higher voltage, and a higher C_D.

Although electrode performance is useful for comparing different active layer structures and materials, to evaluate the viability of our VCNT electrode technology

Table 3 Assumed Parameters for the DLC Energy Density Calculations

Symbol	Description	Value	Unit
A_3	Triple wall nanotube surface area	450	m^2/g
ρ_C	CNT density	0.45	g/cm^3
C_D	CNT specific (differential) capacitance	50	μF/cm^2
F	Faraday constant	96484	C/mole
ρ_{Al}	Aluminum density	2.7	g/cm^3
T_{Al}	Aluminum thickness	15	μm
M	Electrolyte molarity	2.0	mole/l
V_M	Maximum operating voltage	2.7	V
ρ_e	Electrolyte density	0.8	g/cm^3
ρ_S	Separator density	0.8	g/cm^3
π_S	Separator porosity	60	%
T_S	Separator thickness	10	μm
P	Packaging volume and weight (ref. to total cell)	10	%

Table 4 Energy and Charge Stored by Two 1 cm² VCNT Electrodes Along With the Weights and Volumes of the Electrodes and Cell Components With Dimension Described in Table 3

Symbol	Description	Value	Unit
A	Electrode Euclidean size	1	cm²
Q	Total charge stored in a VCNT electrode	2.75	C
W_{Al}	Aluminum weight	4.05	mg
V_{Al}	Aluminum volume	0.0015	cm³
W_S	Separator weight	0.8	mg
V_S	Separator volume	0.001	cm³
W_C	Weight of the CNT active layer	9.08	mg
V_C	Volume of the CNT active layer	0.02	cm³
W_e	Electrolyte weight	23	mg
V_e	Electrolyte volume	0.028	cm³
E_{tot}	Energy stored in two VCNT 1 cm² electrodes	3.72	J

we estimate the achievable energy density of a packaged cell. The parameters used to make this estimation for a DLC cell using two 1 cm² VCNT electrodes are summarized in Table 4, along with the resulting total energy stored in the cell at V_M. The charge, Q, in this table is the ionic charge required for one electrode at a voltage of 1.35 V (half the cell voltage) and a capacitance of 2.04 F ($C_w W_C$).

The energy densities of a cell comprised of two VCNT active layers and aluminum charge collectors, separator, and electrolyte are given by

$$E'_W = \frac{E_{TOT}}{2 \cdot (W_{Al} + W_C) + W_S + W_e} = 23.0 \text{ Wh/kg} \quad (5)$$

$$E'_V = 24.2 \text{ Wh/l}. \quad (6)$$

The weights of each CNT active layer and of the necessary electrolyte are

$$W_C = \rho_C \cdot V_C = 9.08 \text{ mg} \quad (7)$$

$$W_e = \frac{2Q \cdot \rho_e}{M \cdot F} = 23 \text{ mg}. \quad (8)$$

The electrolyte weight, W_e, is calculated based on the assumption that twice the minimum required ion density, Q, is necessary to maintain electrolyte conductivity.

Assuming a weight and volume of the packaging equivalent to 10% of the total cell weight and volume (electrodes, electrolyte and separator), the overall volumetric and gravimetric energy densities are estimated using (9) and (10). These assumptions are realistic when aluminum is used for the cell package

$$E''_W = E'_W \times 0.9 = 21 \text{ Wh/kg} \quad (9)$$

$$E''_V = E'_V \times 0.9 = 22 \text{ Wh/l}. \quad (10)$$

Comparing Table 5 with Table 1 we see that the theoretical gravimetric energy densities of a VCNT-based DLC cell is four times that of a typical commercial ultracapacitor. This improvement is due to the specific capacitances obtainable with our VCNT electrodes in conjunction with a nanotube morphology conducive to electrolyte storage.

The calculated values in Table 5 were based on an assumed maximum working voltage of 2.7 V. However, this

Table 5 Summary of Specific Capacitances and Cell Energy Densities

Symbol	Description	Value	Unit
C_W	Gravimetric active layer specific capacitance	225	F/g
C_V	Volumetric active layer specific capacitance	102	F/cm³
E_W	Gravimetric Energy density for two CNT layers	57	Wh/kg
E_V	Volumetric energy density for two CNT layers	25.8	Wh/l
E'_W	Gravimetric energy density for two CNT electrodes, separator and electrolyte	23	Wh/kg
E'_V	Volumetric energy density for two CNT electrodes, separator and electrolyte	24.2	Wh/l
E''_W	Gravimetric energy density of the packaged cell	21	Wh/kg
E''_V	Volumetric energy density of the packaged cell	22	Wh/l

limitation is due to electrolyte degradation in conventional activated carbon DLCs resulting from contamination during the activation process and from the binder used to attach the carbon to the current collector. The purity of CNTs avoids this contamination, resulting in the ability to operate the device at a working voltage approaching 3.5 V. Keeping volume fixed, the higher voltage would require a higher molarity electrolyte. Under these conditions the energy densities are increased to about 35 Wh/kg and 37 Wh/l.

VII. CONCLUSION

We have shown that long, vertically aligned carbon nanotubes can be grown directly on an aluminum foil current collector. Wetting properties have been shown to be satisfactory for a tube density of $4 \times 10^{11}/cm^2$. A carbon area specific capacitance of 50 $\mu F/cm^2$ has been

demonstrated by others, and together with an anticipated tube density of $10^{12}/cm^2$ and an electrolyte of 2.0 M acetonitrile, energy densities of 21 Wh/kg and 22 Wh/l are projected for a packaged, commercial CNT-based EDLC at 2.7 V. If a molarity of 2.7 for the electrolyte is shown to be practical, the increase in working voltage to 3.5 V results in energy densities of 35 Wh/kg and 37 Wh/l. This is approximately seven times higher than the energy densities available with commercial activated carbon EDLCs. ∎

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