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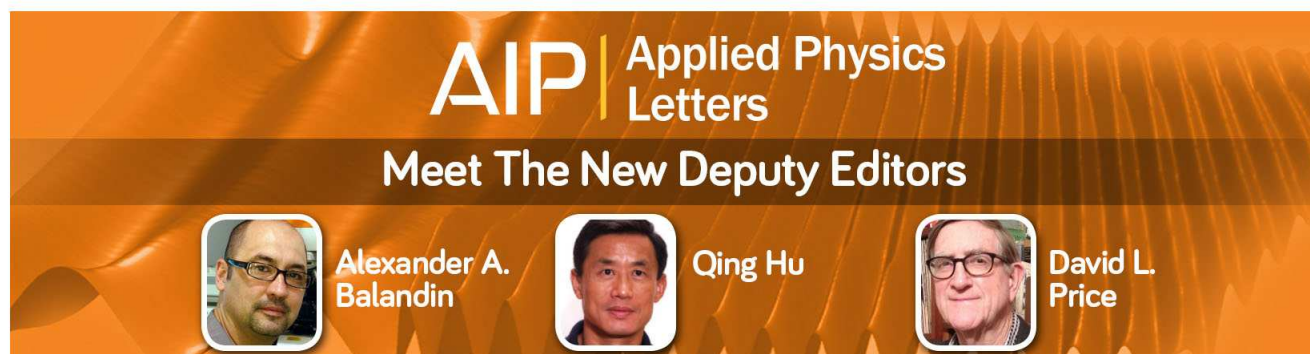
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Roll-to-roll production of spray coated N-doped carbon nanotube electrodes for supercapacitors

Mehmet Karakaya,^{1,2,a)} Jingyi Zhu,^{1,2,a)} Achyut J. Raghavendra,^{1,2}
 Ramakrishna Podila,^{1,2,b)} Samuel G. Parler, Jr.,³ James P. Kaplan,³
 and Apparao M. Rao^{1,2,b)}

¹*Department of Physics and Astronomy, Clemson University, 202 C Kinard Lab, Clemson, South Carolina 29634, USA*

²*Clemson Nanomaterials Center, Clemson University, 81 Technology Dr., Anderson, South Carolina 29625, USA*

³*Cornell-Dubilier Electronic, Inc., Liberty, South Carolina 29657, USA*

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Although carbon nanomaterials are being increasingly used in energy storage, there has been a lack of inexpensive, continuous, and scalable synthesis methods. Here, we present a scalable roll-to-roll (R2R) spray coating process for synthesizing randomly oriented multi-walled carbon nanotubes electrodes on Al foils. The coin and jellyroll type supercapacitors comprised such electrodes yield high power densities ($\sim 700 \text{ mW/cm}^3$) and energy densities (1 mW h/cm^3) on par with Li-ion thin film batteries. These devices exhibit excellent cycle stability with no loss in performance over more than a thousand cycles. Our cost analysis shows that the R2R spray coating process can produce supercapacitors with 10 times the energy density of conventional activated carbon devices at $\sim 17\%$ lower cost. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905153>]

As the growth of portable electrical equipment, electronics, and hybrid electric vehicles continues to accelerate, there is an imminent need for efficient energy storage devices with high energy and high-power densities.¹ Even the most prominent energy systems, such as batteries which can exhibit energy densities as high as 400 mW h/cm^3 , are limited by their slow power delivery ($< 0.1 \text{ W/cm}^3$).² Alternatively, electrochemical double layer capacitors (EDLCs) or supercapacitors can provide high power densities ($\sim 10\text{--}100 \text{ W/cm}^3$) with an extremely long cycle life ($> 10^5$); however, their energy densities are significantly lower than batteries. In EDLC devices, the electrolyte ions are stored on the electrode surface without any chemical reactions allowing a fast charge or discharge. Accordingly, the capacitance of such devices (and in turn their energy density) is mostly dependent on the specific surface area of the electrode. Hence, in the recent years, there has been a concerted effort to increase the energy density of EDLCs through three approaches: (i) the addition of pseudo-capacitance materials where redox materials are added to the EDLC electrodes, (ii) increasing the specific surface area of the electrode by nanosizing, and (iii) preparation of a hybrid electrode based on (i) and (ii). Among the multitude of emerging low-dimensional materials, carbon nanomaterials are considered as one of the ideal electrode materials due to their high electrical conductivity, chemical stability in different solutions (from strongly acidic to basic), and thermal robustness. In particular, EDLC devices with specific capacitances as high as 180 F/g have been realized using carbon nanotubes (CNTs).^{3,4} Although these values are an order of magnitude higher than traditional

activated carbons, two main challenges still persist in realizing EDLC devices with a higher specific energy while retaining the ability to rapidly charge and discharge over multiple thousands of cycles for practical applications: (i) the net capacitance (C_{tot}) of the CNT electrodes is smaller than the predicted values (based on surface area) due to the presence of a series quantum capacitance (C_Q)^{5,6} and (ii) the lack of facile scalable manufacturing methods and high production costs that limit the widespread use of CNT electrodes.⁷ Although some potentially scalable methods such as chemical vapor deposition (CVD),^{8–10} vacuum filtration,¹¹ ink-jet printing,¹² dip-coating,¹³ spray coating, or air-brushing¹⁴ have been reported for producing nanostructured bulk electrodes, they suffer from poor CNT uniformity, delamination issues, and a high contact resistance between CNTs and current collectors.

Here, we address the two imminent challenges described above through a scalable roll-to-roll (R2R) technique for producing N-doped CNT (NCNT) electrodes with higher C_Q and higher energy and power density. Particularly, we show that N-dopants in the CNT structure introduce extra density of states (DOS) at the Fermi level allowing an increase in C_Q and hence the net specific capacitance beyond the limits of pristine CNTs (PCNT). We developed a facile spray coating techniques, that is, amenable for R2R production of randomly aligned networks of pristine and N-doped CNTs at rates as high as $\sim 4 \text{ cm}^2/\text{s}$. More importantly, we show that symmetric supercapacitor cells (coin and jelly roll type devices) consisting spray coated N-doped CNT electrodes exhibit energy density ($\sim 1 \text{ mW h/cm}^3$) comparable to Li-thin film batteries¹⁵ with a relatively high power density ($\sim 0.7 \text{ W/cm}^3$) and > 1000 rapid charge/discharge cycles.

Two different types of pristine multi-walled CNTs (labeled PCNT1 with 15 nm diameter and PCNT2 with 70 nm diameter) and NCNTs (2% nitrogen substituted; 30 nm

^{a)}M. Karakaya and J. Zhu contributed equally to this work.

^{b)}Authors to whom correspondence should be addressed. Electronic addresses: rpodila@g.clemson.edu, Telephone: 864-656-4447 and arao@g.clemson.edu, Telephone: 864-656-6758.

diameter) were acquired from Sai Global Technologies, Inc. Porous aluminum foils with varying thicknesses of 20, 30, 40, and 50 μm (labeled as CD20, CD30, CD40, and CD50) and an average pore size 1 μm were kindly provided by Cornell Dubilier (CD), Liberty, SC. All other chemicals are purchased from Alfa Aesar. For spray coating, CNTs were dispersed in isopropanol (1 mg/ml) using a tip sonicator (1/8 in. tip diameter, Branson 250W) for 30 min. Subsequently, as shown in Fig. 1(a), CNT suspensions were spray coated onto CD aluminum foils using a paint gun (Iwata 5095 WS400) with 1.3 mm nozzle and 29 psi ambient air pressure. From scanning electron microscope (SEM) images of the cross-section of spray coated electrodes (see inset in Fig. 1(a)), the thickness of CNT layer was found to be $\sim 4 \mu\text{m}$ with an areal density of $\sim 0.16 \text{ mg/cm}^2$. The porous structure of our Al foils allows the entrapment of CNTs resulting in a moderately strong adhesion even in the absence of a binder (Figs. 1(b) and 1(c)). Such an entrapment-assisted adhesion allows our CNT electrodes to be easily rolled into jellyroll structures, for producing supercapacitor devices, without any micro-cracks that could disrupt electrode conductivity (Figs. 1(c) and 1(d)).

We measured the electrochemical properties of spray coated CNT electrodes in a three-electrode (CNT working, Ag/Ag⁺ reference, and Pt counter electrodes) configuration using 1M tetraethylammonium tetrafluoroborate (TEABF₄, >99%) in acetonitrile (ACN) in a Gamry reference 3000 electrochemical system. In these experiments, spray coated CNT electrodes on Al foils were fastened in a Teflon cell with an exposed area of $\sim 0.5 \text{ cm}^2$ and were contacted with Ti foil. All CNT electrodes were pre-treated using voltammetric cycling from 0 to 2.0 V at a scan rate of 100 mV/s until the current profile became constant. A typical cyclic

voltammetry (CV) profile (Figs. 2(a)–2(c)) for all our samples did not show the presence of any redox reactions suggesting EDLC behavior. Interestingly, as evident from Fig. 2(c), the net capacitance of NCNT samples was found to be higher than PCNT samples. This increase in capacitance may be rationalized as follows. Previously, Yamada and Bandaru⁵ have suggested that the C_{tot} of nanomaterial electrodes consists of both their C_Q and the double layer capacitance (C_{dl}) in series, i.e., $1/C_{\text{tot}} = 1/C_Q + 1/C_{\text{dl}}$. C_Q depends upon the DOS at the Fermi energy (E_F) and may be quantified as $C_Q = e^2 \text{DOS}(E_F)$. Traditionally, C_Q for CNTs is low because their quasi one-dimensional nature results in van Hove singularities in the DOS structure with vanishing DOS at E_F . It was earlier suggested that the measured capacitance of CNT structures is at least an order of magnitude lower than the expected C_{dl} (from the surface area measurements) due to the presence of lower C_Q in series. The N-doping in CNTs is expected to increase $\text{DOS}(E_F)$ leading to an increase in the C_Q because N dopants can disrupt the CNT lattice and inject an extra lone pair of electrons into the delocalized carbon π -orbitals.⁶ An increase C_Q through $\text{DOS}(E_F)$, arising from N doping, diminishes the $1/C_Q$ component allowing one to harness the true double layer capacitance of CNTs, as shown in Fig. 2(c). The volumetric capacitance was calculated by the following equation:

$$C_{\text{vol}} = \frac{C_{\text{meas}}}{V_e},$$

where C_{meas} is the measured single electrode capacitance. The total volume of the electrode is calculated by $V_e = (T_{\text{Al}} + T_{\text{CNT}}) \times \text{Area of electrode}$, where T_{Al} and T_{CNT} are the thickness of the Al substrate and CNT layer, respectively.

Based on the better performance of NCNT spray coated single-electrodes, we fabricated symmetric EDLC coin cells and jellyroll devices (see Fig. 3(a)) comprised CD20-NCNTs. The highest energy and power density of the CD20-NCNT coin cells in TEABF₄-ACN (with Celgard 2325, 25 μm thick separators) were found to be $\sim 0.75 \text{ mW h/cm}^3$ and 480 mW/cm^3 (data not shown). These energy and power density values are only moderate since the cell voltage is limited to 2 V by the TEABF₄-ACN electrolyte. Accordingly, we repeated our coin cell measurement in an ionic liquid, viz., 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) along with Energain® separator (DuPont) to increase the voltage window of the cell to 3 V. Prior to the coin cell assembly with ionic liquid, each electrode and separator were soaked overnight ($\sim 20 \text{ h}$) in [BMIM][BF₄]. The separator was placed between the two electrodes in a coin cell apparatus (MTI Corp.), as shown in Fig. 3(a). CV profiles of as-assembled coin cell with [BMIM][BF₄] electrolyte were recorded at various scan rates over a cell voltage range of 0 to 3 V, as shown in Fig. 3(b). The Nyquist plot (data not shown) for these coin cells showed that the internal resistance for our CD20-NCNT ($\sim 20 \Omega$) samples is moderately higher than CNTs directly grown on Al electrodes ($\sim 1 \Omega$) in Ref. 8. Such a result is expected since CVD grown CNTs on Al foils are vertically aligned and have negligible inter-tube junction resistance unlike randomly oriented CNTs in the pores of CD20 Al foils.

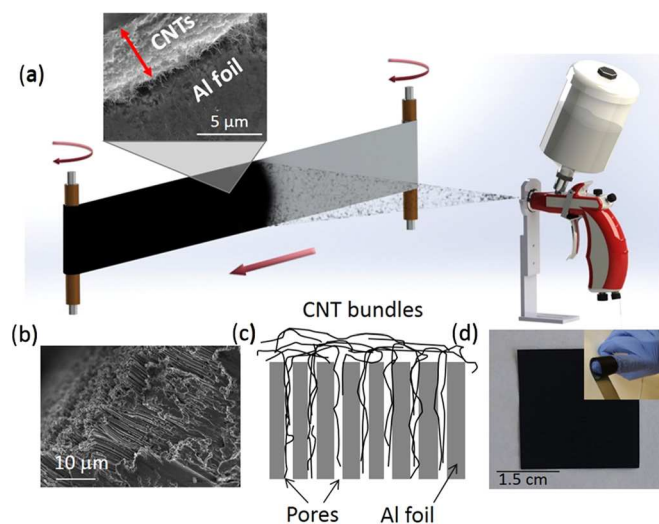


FIG. 1. (a) A schematic of the spray coating set up for roll-to-roll production of carbon nanotube (CNT) coated Al electrodes (inset: scanning electron microscope image of spray coated CNTs on Al foil). (b) Scanning electron microscope cross-sectional image of CD20 Al foil showing the Al channels/pores. (c) Upon spraying, CNT bundles are adsorbed into the Al foils and adhere well without the need of a binder. The electrolyte ions can access high surface area of entangled bundles on the surface to exhibit an increased electrical double layer capacitance. (d) A photograph of an Al electrode after CNT spray coating. The inset shows that the electrodes can be easily rolled without creating any disruption in CNT conduction network.

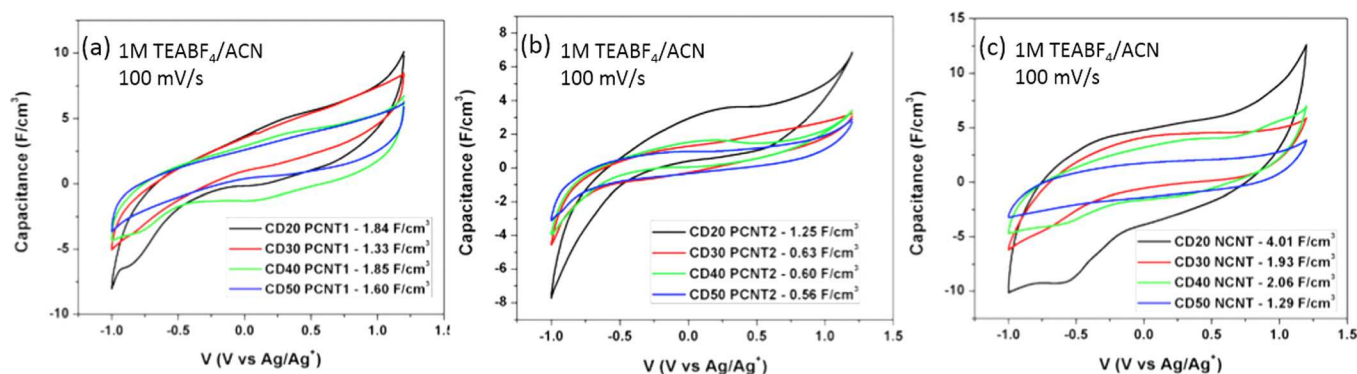


FIG. 2. (a)–(c) Scan rate normalized cyclic voltammetry loops for two types of pristine CNTs (PCNT1 and PCNT2) and NCNTs on CD20 Al foil. Clearly, no redox peaks are observed, indicating that the samples exhibit good electrical double layer capacitor behavior. The net capacitance of NCNTs in (c) is higher compared to PCNT1 and PCNT2 due to an increased quantum capacitance resulting from the presence of N-dopants. Quantum capacitance is directly proportional to the density of electronic states at the Fermi level ($\text{DOS}(E_F)$). N-dopants can increase the $\text{DOS}(E_F)$ by providing additional electrons to the honeycomb carbon lattice, and thereby result in an increase in $\text{DOS}(E_F)$.

The charge–discharge characteristics of CD20-NCNT coin cells at 0.8 and 1 mA are shown in Fig. 3(c). From the discharge measurements, we calculated the energy and power density of the electrodes shown in Ragone plot (Fig. 3(d)) using $W = 1/2 C_{\text{tot}} V^2$, where W is the energy density and V is the cell voltage, and $P = \Delta W / \Delta t$, where P is the power density and Δt is the discharge time. The volumetric specific energy and power densities are calculated by normalizing the W and P value by the total volume of the two electrodes. We observed that the performance of all the EDLC coin cells was stable for over ten thousand cycles with a drop of 12% in performance (Fig. 3(e)). After 10 000 cycles, we recovered the spray coated CNTs and recoated them on the tested Al foil, in other words, we recycled both

the active (CNTs) and current collector (Al foil) materials. As seen in the inset of Fig. 3(e), the recycled supercapacitor coin cell exhibited a drop of $\sim 40\%$ performance but could be run at 60% of the original material performance for another 10 000 cycle, suggesting excellent sustainability of our spray coated electrodes.

As shown in Fig. 3(f), we found that the increase in the cell voltage leads to energy and power densities as high as 1 mW h/cm^3 and 700 mW/cm^3 on par with Li-thin film batteries.² While the coin cells provide excellent platform to test devices in the laboratory, the main challenge is to fabricate supercapacitor devices in the jellyroll form without introducing any micro-cracks that adversely influence the electrode conductivity. Accordingly, we used the CD20-

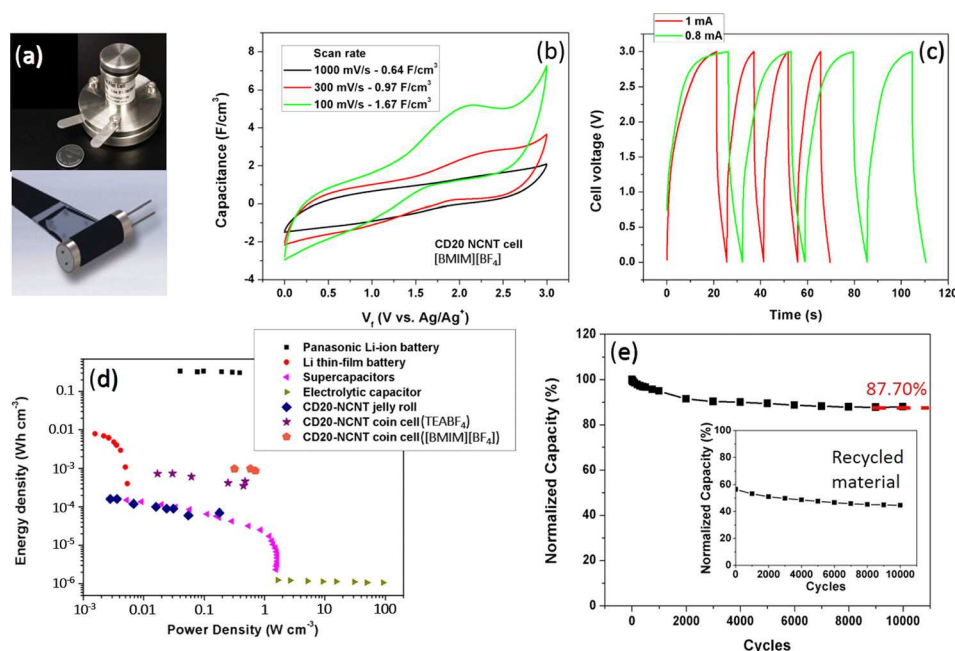


FIG. 3. (a) The top panel shows a coin cell assembly for testing spray coated nitrogen doped carbon nanotube (NCNT) electrodes, while the bottom panel shows the structure of a jellyroll capacitor. (b) Cyclic voltammetry profiles of as-assembled coin cell with electrolyte of $[\text{BMIM}][\text{BF}_4]$. (c) The charge–discharge characteristics of CD20-NCNT coin cells at 0.8 and 1 mA. (d) Ragone plot comparing the performance of CD20 NCNT coin cell and jellyroll devices with $\text{TEABF}_4\text{-ACN}$ and $[\text{BMIM}][\text{BF}_4]$ electrolytes to conventional supercapacitors, Li-thin film batteries, and other energy storage devices (see Ref. 15), and (e) the coin cell device made from CD20-NCNT electrodes exhibited excellent cycle stability with only $\sim 12.3\%$ degradation in performance over 10 000 cycles. After 10 000 cycles, the Al foil current collector and NCNT material were used for the second time to make recycled devices. The recycled device (with recycled electrodes) exhibited 60% specific capacity (see inset) of the as-prepared NCNTs (electrodes in run-1 shown in Fig. 3(b)) indicating excellent material recyclability.

NCNT electrodes to fabricate jellyroll supercapacitor devices and evaluated their performance with the traditional organic electrolyte (viz., TEABF₄-ACN) used in commercial devices, as shown in Fig. 3(f). The energy and power density values for these jellyroll devices are on par with the traditional supercapacitors which use binders to enhance the adhesion of activated carbon to the current collector. Our facile spray coating method (cf. Fig. 1(a)) eliminates the use of binder by using the porosity of Al foils. The spraying rate of this coating system ($\sim 4 \text{ cm}^2/\text{s}$) is an order of magnitude higher than traditional CVD systems and could potentially lead to high-throughput EDLC device manufacturing.

A cost analysis of the supercapacitor coin cells produced in the laboratory by hand has little relevance to their economic performance application since the extrapolations do not scale linearly from lab-production to large-scale manufacturing. Accordingly, in order to estimate industrial large-scale production of supercapacitor cells, up-scaling needs must be included. As reported by Dura *et al.*,¹⁶ the sustaining costs of supercapacitor production (K_{cell}) may be expressed as

$$K_{\text{cell}} = M_i P_{M_i} + E_i P_{E_i} + X_i P_{X_i} + Y_i P_{Y_i}. \quad (1)$$

In Eq. (1), M , E , X , and Y represent the rate of consumption of materials, energy, labor, and maintenance, while P_n ($n = M, E, X$, and Y) is the corresponding price for the considered material, energy, labor, and maintenance for the individual process steps i of the production line. It was previously shown that term 1 in Eq. (1) contributes up to 60% of K_{cell} , leaving the other three terms sum up to 40%. Traditional supercapacitor production is a 12 step process (each step contributing $\sim 3.5\%$ to K_{cell}) wherein 5 steps involve electrode production (viz., mixing active material with binder, coating, calendaring, slitting, and drying), while 7 steps are necessary for the cell assembly.¹⁶ Considering that our electrode production involves three-step process (sonication, spraying, and drying), we expect that the production costs are reduced by $\sim 7\%$ in our process. Furthermore, our spray coating process also eliminates the

use of binder materials that contribute $\sim 10\%$ of the materials cost. Overall, using our approach, the cost of rolling a jellyroll capacitor can be reduced by $\sim 17\%$. More importantly, conventional supercapacitors containing activated carbon provide energy densities only as high as $\sim 0.1 \text{ mW h/cm}^3$. Considering that NCNT electrodes can reach an order of magnitude higher energy densities (cf. Fig. 3(e)), our method clearly demonstrates that CNT supercapacitors with 10 times higher energy density could be produced at 17% lower cost compared to conventional devices.

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