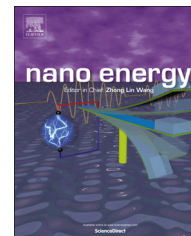




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RAPID COMMUNICATION

Roll-to-roll synthesis of vertically aligned carbon nanotube electrodes for electrical double layer capacitors



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Abstract

Research in carbon nanomaterials has seen tremendous growth in recent years; however, technological advances are limited by the lack of continuous and scalable synthesis methods. Here we present a scalable roll-to-roll process for synthesizing vertically-aligned multi-walled carbon nanotubes (VACNTs) on Al foil ribbons which are continuously drawn through a chemical vapor deposition (CVD) reactor operating at ambient pressure and a relatively low growth temperature (600 °C). Electrodes comprised of VACNT forests synthesized in this process are directly assembled into supercapacitor cells, which yield high power densities (1270 W/kg) and energy densities (11.5 Wh/kg). These devices exhibit excellent cycle stability with no loss in performance over more than a thousand cycles.

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Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, have emerged as a promising solution for applications requiring durable and reliable devices with high power and energy density [1,2]. EDLCs offer comparable power densities to electrolytic capacitors while providing 2 to 3 orders of magnitude increase in energy density, thus allowing them to complement or serve as possible replacements for existing batteries [3]. Due to the prevalent use of activated carbon electrode materials, EDLC performance is often correlated with the electrode surface area, in which pore size distribution and the solvated electrolyte ion radius define the accessibility [4]. In this regard, the unique properties of carbon nanotubes (CNTs) make them suitable candidates for EDLC electrodes [5]. While the electrochemical stability of CNTs is necessary for long lifetime EDLCs, their high electrical conductivity allows for better electron transfer to the current collector and their high surface-to-volume ratio provides greater ion access [4]. Accordingly, vertically aligned arrays of multi-walled CNTs (VACNTs) have been considered for use in EDLCs due to their facile synthesis and the ability to control the ion-accessible surface by varying the CNT areal density on growth substrates [6–10]. VACNT electrodes have been used to achieve high power density EDLCs [11]; however, continuous synthesis methods to prepare VACNTs directly on current collectors (e.g., Al foil) at relatively low costs are needed for commercially viable high power and high energy density EDLCs. Additionally, when CNTs are grown from catalyst particles that are adhered to the current collector, the need for a binder is eliminated, thereby reducing inactive weight and contact resistance [4].

Although CNTs can be synthesized in large quantities, present processes are not amenable for VACNT growth directly on current collectors for scalable manufacturing of EDLC electrodes [12]. Since the discovery of CNTs, several methods have been pioneered for their production, including electric arc discharge [13,14], laser ablation [15,16] and chemical vapor deposition (CVD) [17,18], however, only CVD has emerged as a practical and reliable method for synthesizing VACNT forests. While the CVD method is relatively versatile in terms of controlling CNT characteristics (e.g., tube diameter, number of walls, and dopant ratio) [19,20], three factors that limit large scale VACNT synthesis are: (i) substrate size set by reactor geometry, (ii) requirements of a complex catalytic substrate preparation, and (iii) high operating temperatures that are incompatible with traditional current collectors (e.g., Al foil).

Previously, Andrews et al. developed a ferrocene-xylene liquid injection floating catalyst technique to grow VACNT forests on bare SiO₂/Si or quartz substrates, greatly simplifying the synthesis process [21]. Considering the startup and shut-down times for batch processing (which often consume >95% of runtime), a continuous roll-to-roll (R2R) process is expected to greatly reduce time, energy, and cost needed to produce VACNT forests [22]. Here, we describe a commercially viable low temperature R2R process for growing VACNTs on inexpensive Al foil current collectors to achieve continuous production of CNT-based EDLC electrodes. Our electrochemical studies on single electrodes show that VACNT forests produced using our R2R method exhibit nearly four-times higher capacitance (~50 F/g) than randomly entangled buckypapers prepared

from commercial CNTs (~13 F/g). Additionally, VACNTs produced using our R2R method displayed significantly lower contact resistance compared to CNT buckypapers. More importantly, we observed that symmetric supercapacitors comprised of R2R-produced VACNT electrodes exhibited high power densities (1270 W/kg) and energy densities (11.5 Wh/kg) with no loss in performance over more than a thousand cycles, compared to CNT buckypapers (650 W/kg and 5 Wh/kg).

Materials and methods

Tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%) and tetraethylammonium tetrafluoroborate (TEABF₄, >99%) were purchased from Sigma Aldrich. Acetonitrile (Certified ACS) and propylene carbonate (99%) were obtained from Fisher. O-xylene (98%) and ferrocene (98%) were purchased from Sigma Aldrich. Al foil substrates were purchased from Aldrich (99.9%) or from the local grocery store (Reynolds). Multi-walled Carbon Nanotubes (30–50 nm outer diameter) were purchased from CheapTubes.com. Celgard separators (2325, 25 µm microporous trilayer PP/PE/PP membrane) were provided by Celgard.

Stationary CVD process

VACNT arrays were grown by CVD in a quartz tube with diameter of 2". Both ends of the tube were closed with stainless steel end-caps. The tube was placed in a furnace with two heating zones (reacting zone-40", and preheating zone-20"). A programmable syringe pump was used to inject the precursor (ferrocene in xylene, 0.5 at% Fe), with the tip of the injection nozzle located at the center of the preheating zone. Al foils (Reynolds Wrap, 2 cm × 15 cm) cleaned with acetone were placed in the center of the reacting zone of the furnace. The system was heated up to 600 °C under a flow of Ar (500 sccm)/H₂ (100 sccm). At 600 °C, the precursor was injected into the tube at a rate of 1.5 ml/h, along with C₂H₂ (30 sccm).

R2R process

VACNT arrays were grown using ambient pressure CVD in a Lindbergh Blue tube furnace that has an active zone of approximately 24 cm. The Al foil (Reynolds Wrap) which is used as the substrate is first swabbed clean with acetone. Al foil ribbon is then threaded through the quartz reaction tube and attached to the uptake spool before allowing the system to heat to 600 °C under 500 sccm of Ar. Once the reaction temperature (600 °C) was reached, the uptake motor was activated to reel the foil at a rate of 0.5 cm/min. H₂ and C₂H₂ are then introduced at 50 sccm and 30 sccm respectively, as well as the precursor solution of 0.5 wt% ferrocene in xylene, which was injected into the tube at 0.3 ml/h using a programmable syringe pump (New Era NE-1000).

Preparation of CNT buckypapers (BP)

CNTs (CheapTubes.com) were dispersed in 1% aqueous solution of sodium dodecyl sulfate (SDS) using a tip sonicator

probe (1/8" diameter, Branson 250) with a power of 75 W for 15 min. Subsequently, the suspension was poured onto a polyamide filtration membrane (Whatman, 0.45 μm pore diameter) and filtered using a vacuum filtration setup (Synthware Filtration Apparatus, Kemtech America). The filtrate on the supporting filter membrane was washed with distilled water several times, and then oven dried at 60 $^{\circ}\text{C}$ for 8 h. The resulting film was peeled off the membrane to yield a freestanding CNT electrode.

SEM

The surface morphology of the films was observed using scanning electron microscopy (SEM, Hitachi SU-6600) with an accelerating voltage of 20 kV.

Carbon content

Prior to electrochemical characterization, substrates were cut with dimensions of 1.1 cm \times 1.4 cm and weighed in a balance (Ohaus Discovery Semi-Micro Balance, 0.01 mg). The mass of carbon on each unique sample was calculated after electrochemical characterization by mechanically removing the carbon from the aluminum substrate and weighing the aluminum substrate after drying at 90 $^{\circ}\text{C}$.

Electrochemical analysis

Each sample was characterized in electrolyte solutions using cyclic voltammetry (CV) (1000, 300, 100 mV s^{-1}), galvanostatic charge/discharge cycles and electrochemical impedance spectroscopy (EIS) (0 V DC bias, 0.1–10000 Hz, 10 mV RMS). The CV current was normalized by scan rate (ν) and either substrate area to give F/cm^2 or carbon mass to give F/g . Two analytical systems were used for electrochemical characterization: (1) a 3-electrode Teflon cell for single electrode evaluation and (2) a 2-electrode cell for symmetric supercapacitor testing (MTI Corp). In the 3-electrode cell, the VACNT on Al foil substrates were fastened in a Teflon cell and contacted to the potentiostat (Princeton Applied Research VersaSTAT 4) leads with a Ti foil contact. A silver/silver ion electrode (Ag/Ag^+) was used as the pseudoreference electrode and a Pt mesh was used as the counter electrode. CV and galvanostatic charge discharge

was carried out in the range of -1 to 1.3 V (up to 2 V). In the coin cell apparatus (2-electrode cell), EDLC devices were tested using symmetric samples as the electrodes separated by a Celgard (2325) trilayer separator. In this set up, one of the carbon samples is designated as the working electrode and the other designated as the reference/counter electrode. The cell performance was evaluated using CV, EIS and galvanostatic charge discharge measurements over a cell voltage range of 0–2.3 V.

Results and discussion

We developed a R2R process to synthesize VACNTs directly on a continuously drawn Al foil substrate (~ 2 cm wide, 0.63 mil thick) using the floating catalyst ferrocene-xylene method at a rate of 0.5 cm/min (see Figure 1). At this rate, any given section of the foil has a reactor residence time of ~ 20 min, resulting in the growth of a forest containing 50 μm tall VACNTs (Figure 1c). As the foil is drawn through the slotted end caps of the CVD reactor, a solution of ferrocene in xylene (0.5 at% Fe) is injected through the inlet nozzle at a rate of 0.3 ml/h in the presence of Ar, C_2H_2 and H_2 gases (500, 30 and 50 sccm, respectively). For comparison, VACNT electrodes were also prepared in a stationary CVD process by placing a long (15 cm \times 2 cm) strip of Al foil at the center of a quartz tube and applying similar reaction conditions as described above for the R2R process but with closed end caps. In the stationary and continuous CVD processes, we utilize a relatively low growth temperature of 600 $^{\circ}\text{C}$, which is safely below the melting point of aluminum (no changes in mechanical properties were observed on the Al foil). Also, we used commercially-available CNTs to prepare buckypapers containing randomly oriented nanotubes [23]. For ease of discussion, samples are labeled as follows: (i) R2R process VACNTs (R2R), (ii) stationary CVD process (sCVD), and (iii) buckypapers (BP).

In the stationary CVD process, the amount of CNTs grown depends on the runtime and substrate location relative to the injection nozzle (Figure 2a) due to the depletion of the precursor towards the downstream end of the furnace. We identified nearly uniform growth areas (see substrate locations 1–8 in Figure 2a inset) with CNT height ~ 50 μm (see Figure 2d inset) and measured their electrochemical performance of each electrode type in three different electrolytes to determine optimal electrolyte properties (Figure 2b–d). It is worth

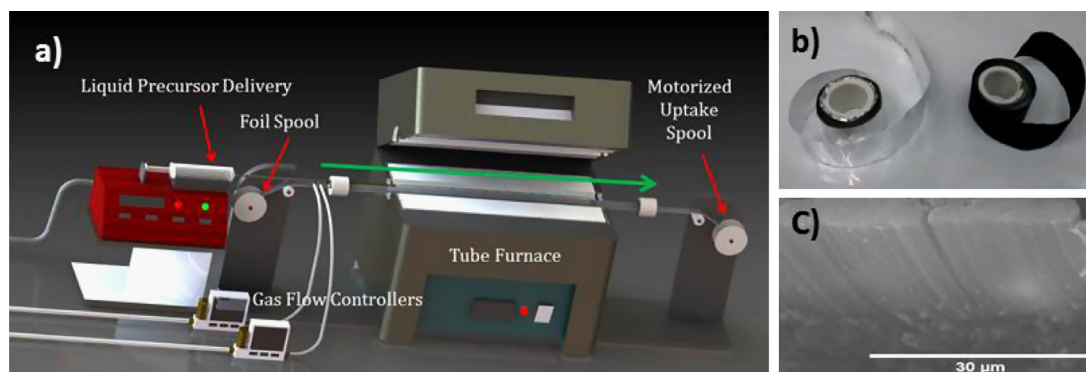


Figure 1 (a) A schematic of the R2R process for growing vertically aligned CNTs on Al foil. (b) Al foil spools before and after CNT growth in the R2R process. (c) A typical scanning electron microscopy (SEM) image of R2R-grown VACNTs.

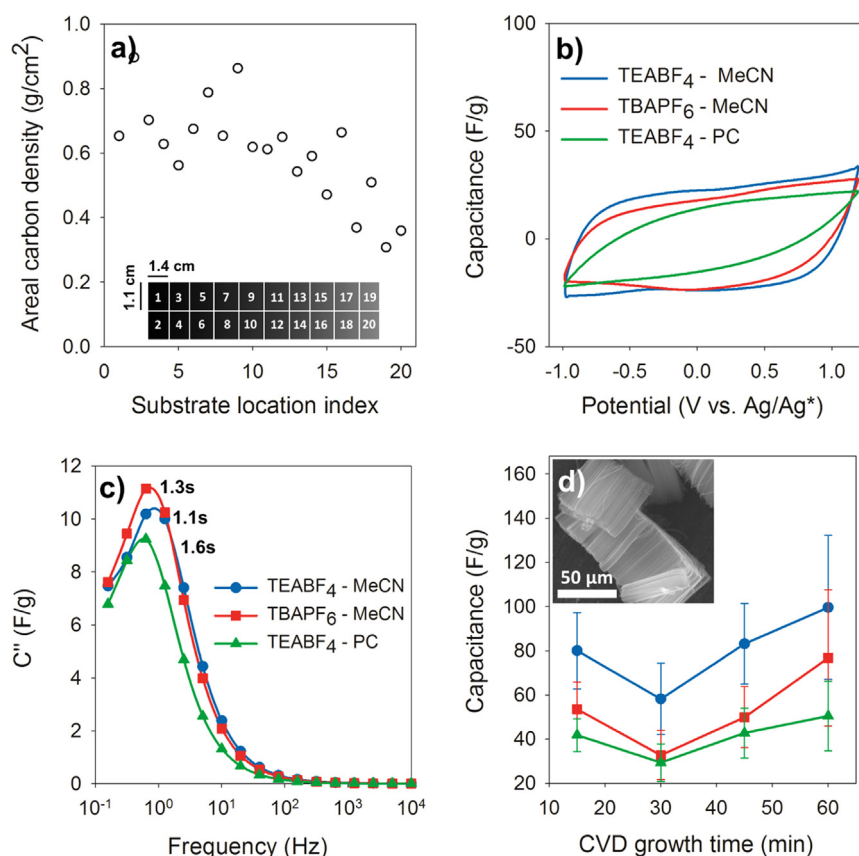


Figure 2 (a) The spatial distribution of VACNT areal density in sCVD samples, (b) CV profiles measured at a scan rate of 1000 mV/s in a standard three-electrode configuration with various electrolytes, (c) Bode plots of the normalized imaginary capacitance (C'' /g) vs frequency for sCVD samples in the three electrolytes, and (d) normalized capacitance vs. voltage profiles ($\nu = 100$ mV/s) for sCVD samples grown for 15, 30, 45, and 60 min (bars represent combined error from mass and CV data). The inset in panel d is a representative SEM image of sCVD VACNT forest grown for 1 h.

noting that aqueous solutions (acidic or basic) are incompatible with Al foil substrates and therefore were not used.

The electrochemical properties of CNT electrodes were initially characterized using cyclic voltammetry (CV) and electrical impedance spectroscopy in a three-electrode configuration to determine the single electrode properties as a function of CNT growth time and electrolyte type. CV profiles were recorded at various scan rates and normalized by scan rate and mass to obtain specific capacitance (F/g) of the VACNT electrodes. The effect of the electrolyte type is apparent in Figure 2b, which shows the normalized CV profiles (1000 mV/s) for sCVD samples grown for 1 h in various electrolytes. The higher conductivity of the organic salts in acetonitrile (MeCN) compared to propylene carbonate (PC) and the smaller ion size of TEABF₄ (~0.45 nm) relative to TBAPF₆ (~0.8 nm) led to the highest specific capacitance of 102 F/g in TEABF₄-MeCN. Slight non-idealities are observed in the CV profiles, which can be attributed to the weak (broad) redox peak of the Fe catalyst (~0.5 V) in the VACNT electrode, and the use of MeCN on Al foil, which leads to more noticeable electrode polarization effects compared to PC.

Impedance analysis verifies the superior performance of the TEABF₄-MeCN solution over the other electrolytes. Due to the nature of the ion-adsorption and ion-diffusion processes within a carbon electrode, each material exhibits

a strong frequency dependent capacitance. On short time scales (high frequency), ions can only accumulate on the outermost surface of the polarized electrodes, whereas on long time scales (low frequency), ions have sufficient time to diffuse into the pores of the electrodes. The Bode plot of the imaginary component of the capacitance (C'') vs. frequency (f) showed that the sCVD samples exhibited shortest relaxation time ($\tau_0 = 1/f_{peak}$) in TEABF₄-MeCN, indicating the fastest discharge process (Figure 2c) [24,25]. At low (high) frequency, capacitance (resistance) dominates the impedance of the circuit and a crossover occurs at f_{peak} . Thus, τ_0 can be used as a factor of merit for supercapacitors and may be interpreted as the minimum time to discharge 50% of the total energy [26].

The influence of CNT growth time on the specific capacitance is shown in Figure 2d, which shows an initial decrease, followed by a steady increase in capacitance with growth time. The higher capacitance values obtained for electrodes grown for 15 min is attributed to the capacitive contribution from the underlying Al foil that is not completely covered by VACNTs, and the possible error in measuring the mass of small amounts of VACNTs. For longer growth times, the increasing specific capacitance with mass arises from an increase in CNT areal density, which in turn affects the accessible surface area. Indeed, when normalized by the areal density, sCVD samples exhibited a linear

increase in specific capacitance (see supplementary information Figure S1).

Using the best conditions determined on sCVD electrodes in terms of VACNT growth time (1 h) and electrolyte type ($\text{TEABF}_4\text{-MeCN}$), we compared the electrochemical performance sCVD, R2R, and BP electrodes at a scan rate of 100 mV/s (Figure 3a). Electrodes prepared at low temperature (600 °C), whether stationary (sCVD) or in the continuous R2R process (R2R), exhibited notably improved performance (51 F/g) compared to BP electrodes with randomly oriented CNTs (13.6 F/g). As shown in Figure 3b, sCVD and R2R electrodes show a linear dependence of current on scan rate, indicative of an ion-adsorption controlled energy storage mechanism. BP electrodes, however, exhibited a linear dependence of current on square root of scan rate (Figure 3b inset), indicating an ion-diffusion controlled process, which may be due to the thickness of the electrodes. Consistent with the CV analysis (cf. Figure 3a), galvanostatic discharge measurements (Figure 3c) show a similar trend in performance with CNT electrode type, where sCVD electrodes had the highest charge capacity of 36.7 mAh/g and R2R and BP electrodes showed values of 24.8 and 13.6 mAh/g, respectively.

Although the charge capacity of R2R electrodes is slightly lower relative to sCVD samples, they exhibit notably faster

discharge times as reflected by their lower time constants (630 ms vs 1.26 s) determined from the Bode plots of C'' vs frequency. Furthermore, the Nyquist plot of the electrical impedance measurements (see supplementary information Figure S2) showed that sCVD and R2R samples display a relatively low internal resistance compared to BP electrodes as the CNTs are directly grown from the current collector surface.

Symmetric EDLC cells were fabricated using electrodes comprised of each type of VACNTs. Prior to cell assembly, each electrode and separator (Celgard 2325, 25 μm thick) were soaked overnight (~ 20 h) in the $\text{TEABF}_4\text{-MeCN}$. The separator was placed between the two electrodes in a coin cell apparatus (MTI Corp), as shown in Figure 4a. CV profiles were recorded at various scan rates over a cell voltage range of 0 to 2.3 V, which are shown for R2R cells in Figure 4b. From the specific capacitance plots shown in Figure 4c, sCVD and R2R samples show similar electrochemical properties with a notably higher specific capacitance than BP electrodes. As observed in the single electrode measurements (cf. Figure S3), the Nyquist plot for EDLC cells (Figure 4d) shows significantly lower internal resistance for sCVD and R2R samples compared to BP electrodes because the CNTs are chemically bound to the substrate rather than simply placed in physical contact.

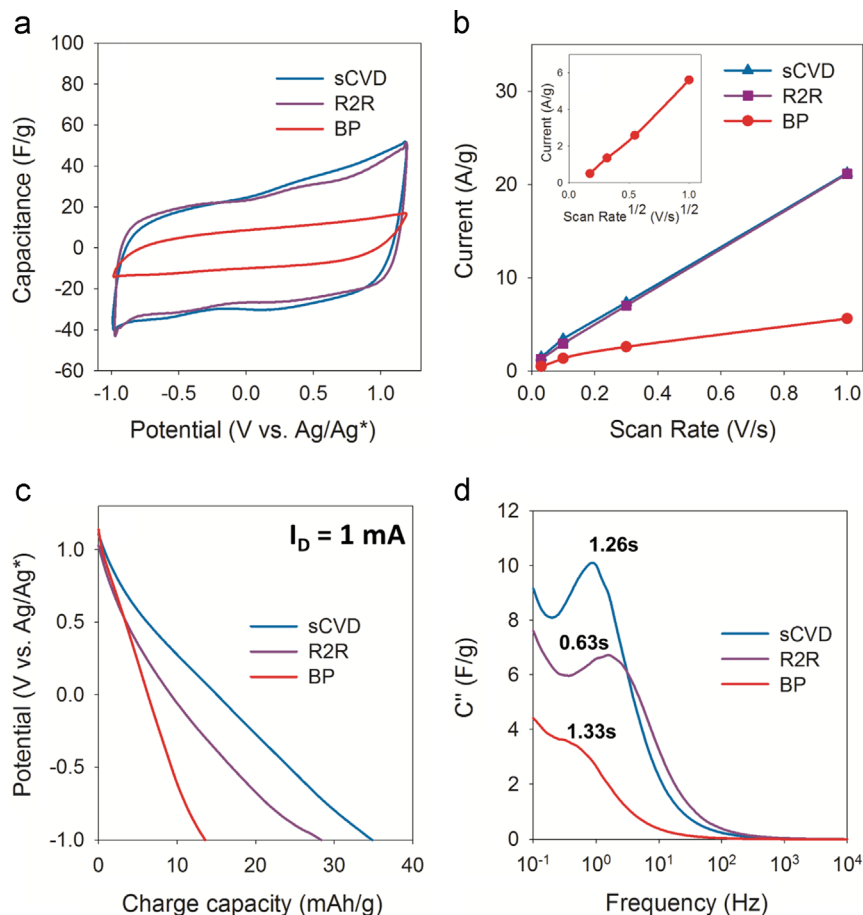


Figure 3 Electrochemical properties of single electrodes comprised of sCVD, R2R, and BP samples. (a) Cyclic voltammograms of various CNT electrodes in $\text{TEABF}_4\text{-MeCN}$ electrolytes normalized by mass and scan rate (300 mV/s). (b) Normalized peak current (I_p) vs scan rate (v) (inset: I_p vs. $v^{1/2}$ for BP electrodes), (c) Galvanostatic discharge profiles (discharge current (I_d) = 1 mA) in $\text{TEABF}_4\text{-MeCN}$, and (d) Bode plots of normalized imaginary capacitance (C'' /g) vs. frequency for the three electrodes.

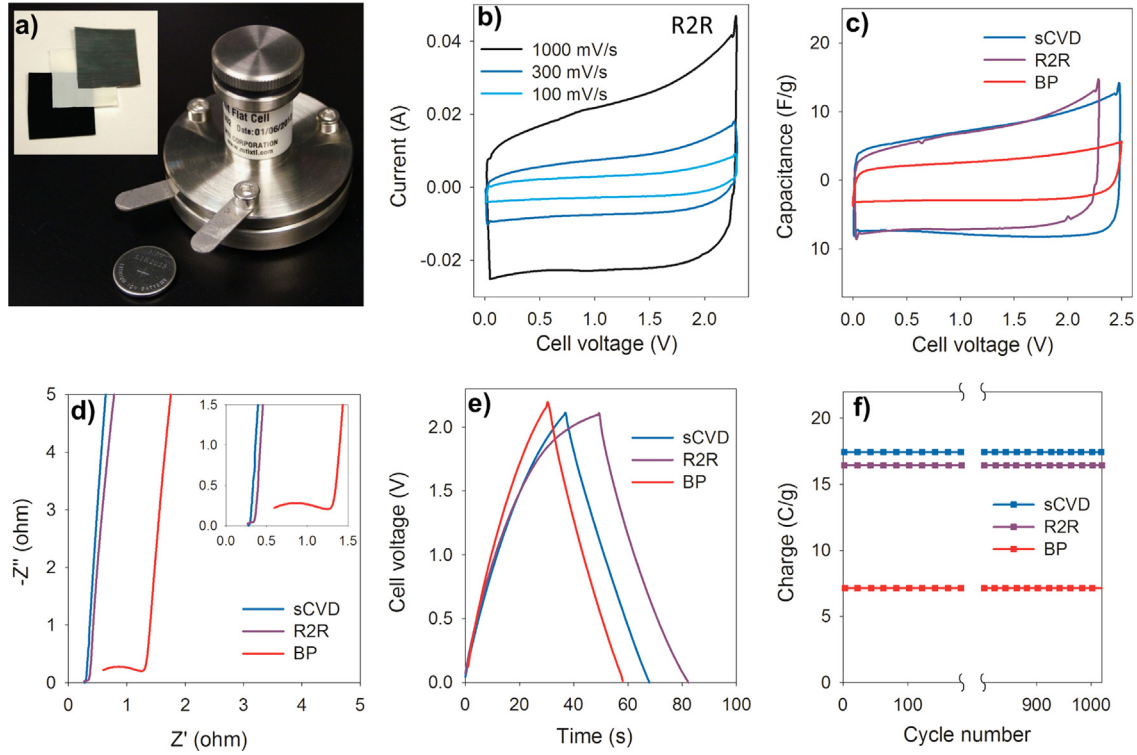


Figure 4 Electrochemical characteristics of symmetric EDLC cells comprised of VACNT electrodes. (a) Photograph of the coin cell apparatus (inset: CNT electrodes and separator), (b) cyclic voltammetry characteristics of and EDLC containing R2R electrodes at various scan rates, (c) normalized CV profiles (F/g) for devices containing different CNT electrodes measured at a scan rate of 1000 mV/s, (d) Nyquist plot for each of the devices described in (c), (e) charge-discharge measurements (1 full cycle at ± 2 mA) for the devices consisting of sCVD (3.4 mg), R2R (3.2 mg), and BP (6.5 mg) electrodes, and (f) charge capacity of each device as a function of cycle number for more than 1000 cycles.

The charge-discharge characteristics of EDLC cells containing different CNT electrodes with the same applied current (~ 2 mA) are shown in Figure 4e. Each cell displays a similar discharge profile; however, devices comprised of the VACNTs from the R2R process showed higher electrode polarization upon charging to the full-charge potential, possibly due to slight differences in electrode masses across the cell. It is difficult to determine the electrode mass prior to testing since the mass is determined by physically separating CNTs from Al foil, preventing us from fabricating a truly symmetric capacitor. When these discharge characteristics are normalized by mass and current (Figure 4e), we observe a similar trend in capacity as in the single electrode measurements, with the highest charge capacity of 9.55 mAh/g observed in the R2R samples and 9.13 mAh/g in sCVD samples. From the discharge measurements, the energy and power density of the electrodes were calculated (Table 1) using the following equations:

$$W = \frac{1}{2} CV^2 \quad (1)$$

where W is the energy density, C is the device capacitance and V is the cell voltage, and

$$P = \frac{\Delta W}{\Delta t} \quad (2)$$

where P is the power density, and Δt is the discharge time. The specific capacitance of the devices was calculated from

the cyclic voltammetry measurements using the following equation:

$$C_{sp} = \frac{\int I dv}{2 \Delta V m v} \quad (3)$$

where I is current, ΔV is the voltage range, m is the carbon mass, and v is scan rate (100 mV/s). As expected, we found good agreement between the single electrode capacitance values determined above, which are approximately 4 times the device capacitance (a device with 2 electrodes has half the capacitance and twice the mass). Lastly, we observed that the performance of all the EDLC cells was stable for over multiple thousand cycles without any degradation (Figure 4f). We expect that these devices remain stable for many thousands of cycles comparable to other inert carbon-based EDLCs.

Conclusion

We have demonstrated a relatively low cost R2R process to synthesize VACNT electrodes directly on Al foils at a low temperature (600 °C) using a ferrocene-xylene solution-based method. Our R2R synthesis method is able to produce VACNTs on Al foils with comparable electrochemical performance to the stationary batch process. EDLC cells assembled with electrodes from the R2R process exhibited the highest performance in terms of capacitance (9.6 F g⁻¹), energy density (11.5 Wh

Table 1 Performance metrics of symmetric EDLC cells.

Carbon (type)	Capacitance (F/g)	Power (W/kg)	Energy (Wh/kg)	τ_0 (s)
R2R	9.6	1270	11.4	0.040
sCVD	9.1	1210	10.2	0.032
BP	4	650	4.9	0.130

kg⁻¹) and power density (1270 W kg⁻¹), which were significantly higher than cells comprising BP electrodes (650 W/kg and 4.9 Wh/kg). Each device demonstrated excellent cycle stability with no loss in performance over more than a thousand cycles suggesting R2R as a viable process for large scale manufacturing of EDLC electrodes.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2014.05.004>.

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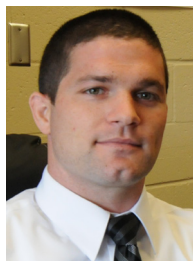
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devices to chemical sensors