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A comparison of single-wall carbon nanotube electrochemical capacitor electrode fabrication methods

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Carbon nanotubes (CNTs) are being widely investigated as a replacement for activated carbon in supercapacitors. A wide range of CNT specific capacitances have been reported in the literature based on experiments using different CNT materials, fabrication methods, and characterization routines; making it difficult to draw conclusions about the relative merits of the different fabrication methods. This work systematically compares four solution-based electrode fabrication methods (drop casting, air brushing, filtration, and electrospraying) and, to a lesser extent, some solution preparation techniques to determine if there is an optimum method for fabricating electrochemical capacitor electrodes out of single-wall CNTs (SWCNTs). We have found that it is best to use CNT solutions free from additives that may be difficult to remove from the fabricated electrode. In addition, the CNT solution preparation (e.g., dilution and sonication) had little effect on the resulting specific capacitance. Large differences in performance due to the fabrication methods were not seen, and the differences that were seen could be ascribed to material loss or contamination during the deposition. A single-layer graphene electrode was also fabricated and tested to obtain an estimate of the specific capacitance potentially achievable with SWCNTs, with 550 F/g demonstrated using 1 molar (M) sulfuric acid.

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1. Introduction

Electrochemical capacitors, also referred to as supercapacitors, have several advantages over conventional batteries, including higher specific power (~2 orders of magnitude higher), higher cycle life (millions of charge/discharge cycles), rapid charge/discharge times (seconds to minutes), high efficiencies (up to 98%), and unaltered performance in extreme heat and cold (1). However, electrochemical capacitors have low energy density compared to batteries which is a significant disadvantage for energy storage. Increasing electrochemical capacitor energy and power densities will make them more useful for portable power applications.

An electrochemical capacitor consists of two solid dielectric-free electrodes, in contact with an electrolyte, which store charge by adsorption of ions onto the electrodes. The capacitance due to the adsorption of ions onto the electrodes is referred to as electrochemical double-layer capacitance, since there is a layer of ions on the electrode with a second layer of counter-ions (oppositely charged ions) next to the adsorbed ions. Energy can also be stored through reduction and oxidation (redox) reactions at the electrodes, whose rates are potential dependent. This type of energy storage is referred to as pseudocapacitance since it behaves electrically as a capacitance, though the charge transfer reactions are more like that of a battery. Since there is no dielectric on the electrochemical capacitor electrodes, the applied biases must remain low enough that electrochemical breakdown of the electrolyte does not occur. This limits the voltage rating on individual electrochemical capacitor cells to ~1 V when using aqueous electrolytes, and ~2.7 V when using organic electrolytes.

Electrochemical capacitors achieve large capacitances by using electrodes with very large surface areas. Carbon electrodes are desirable because they are conductive and have high surface area, good corrosion resistance, and good thermal stability [1]. Carbon materials with improved surface area may increase the capacitance of electrochemical capacitors. Two materials being studied for this are CNTs and graphene. Graphene is a single atomic layer of graphite. Similarly, a SWCNT is a single atomic layer of graphite that curves back on itself to form a tube. Multi-wall carbon nanotubes (MWCNTs) are carbon nanotubes that are more than one atomic layer thick and they were not used in this study. This study focused on SWCNTs since they have the largest surface area to mass ratio given that any interior walls in a MWCNT contribute mass but not surface area. Extremely large capacitances may be obtainable if these materials can be assembled in a manner that optimizes the electrode surface area that is accessible to the electrolyte.

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This study details investigations of various solution-based electrode fabrication methods to determine if there is an optimum method for fabricating SWCNT electrodes for electrochemical capacitors. Solution-based processing was chosen, as it is manufacturable and compatible with roll-to-roll processing. It also does not impose significant thermal and chemical constraints on the underlying current collector as direct growth methods at 900 °C in a reducing environment would. When SWCNTs are deposited from solution, they typically do so in bundles. It is not yet clear if this bundling is detrimental to the resulting accessible surface area and, therefore, the resulting capacitance. In addition, the deposition method may also affect the porosity of the electrode, which will affect how easily the electrolyte ions can move into and out of the electrode (the Warburg impedance) during the charge/discharge process.

Many CNT solution-based processing approaches have been demonstrated with measured specific capacitances of 23–200 F/g reported [2–9]. It is difficult to draw direct comparisons from these studies because they use different: CNT sources including single- and multi-walled tubes, solution compositions, fabrication methods, and characterization protocols. According to Stoller and Ruoff: "Methodology to reliably measure a material's performance for use as an ultracapacitor electrode is not well standardized with various techniques yielding widely varying results" [10]. In addition, many of the higher specific capacitances reported likely include pseudocapacitive contributions in the measured specific capacitance. Such pseudocapacitance contributions may overwhelm the double-layer capacitance, which is the focus of this work, as double-layer capacitance is a measure of the accessible CNT surface area being produced by the fabrication methods tested. We have systematically investigated the individual contributions of the solution preparation and the deposition methods to the achieved double-layer capacitance.

In order to determine how high a capacitance might be achieved with SWCNTs, a model system of a single-layer graphene electrode on sapphire was tested. A dielectric substrate is used to eliminate any contribution to capacitance from the substrate. This should be a reasonable model for SWCNTs since the electrolyte can only access one side of the graphene (corresponding to the outside of a SWCNT).

2. Experimental

Two commercial sources of SWCNTs were used in this work. The use of binders or conductivity enhancers as is typical with activated carbon electrodes has been avoided here as they were deemed unnecessary and it was feared they would complicate the analysis. For a comparison of surfactant-free and surfactant-containing solutions, chirally pure (6,5) SWCNT powder was obtained from Sigma–Aldrich. That pure semiconducting CNTs were used is of no significance to the experimental results reported here. The CNT powder based solutions were made by mixing approximately 1 mg of CNTs with 5 ml of water and probe sonicating for 10 min at 20% amplitude using a Sonics and Materials model VCX 130 probe sonicator. Two solutions were made, one without surfactant, and one with 100 μl of CNTsperse AQ surfactant purchased from www.MKnano.com. These two solutions were allowed to sit for 10 min to allow any large particles to settle to the bottom before the top 4 ml were vacuum filtered using 0.4 μm HTTP filters from Millipore. After filtering, the resulting CNT mat was washed by filtering an additional 75 ml of DI water. Commercially obtained CNT solutions in acetone were also investigated. These solutions consisted of functionalized or unfunctionalized SWCNTs suspended in acetone, using surfactants and/or dispersants containing: a-(nonylphenyl)-hydroxy-branched poly(oxy-1,2-ethanediyl)(20–50%); 2,4,7,9-Tetramethyl-5-decyne-4,7-diol (2–10%); and 2-Butoxyethanol (<1%); and other proprietary components. These filtered CNT mat electrodes were mounted in a polycarbonate holder that pressed a nickel wire against the CNT mat to serve as a current collector, and they were characterized using 1 M potassium hydroxide electrolyte, a nickel foil counter-electrode, and a silver/silver chloride pellet reference-electrode.

For the experiments comparing CNT deposition methods, a surfactant-free SWCNT solution in water was obtained from Brewer Science Inc. and used as-received or diluted 1:3 with ethanol. These solutions were used with or without 10 min probe- plus 30 min bath-sonication. The Brewer Science Inc. solution contains SWCNTs that were functionalized by refluxing them in strong acids, and it is sold for spin coating films of individual SWCNTs. The functionalization results in sufficient CNT solubility in water that an approximately 70 μg/ml concentration can be achieved without the aid of surfactants. 1 ml of the solution (4 ml if diluted with ethanol) was deposited using four different methods onto 2 cm × 2 cm sections of titanium foil on a 175–200 C hotplate (except for the filter and transfer method which is done at room temperature). Drop casting was performed by depositing 10's of μl (∼mm diameter droplets) at a time onto the current collector and letting it dry before repeating; airbrushing deposited droplets 10's of microns in diameter which form a quasi-continuous thin film which was allowed to dry before continuing spraying; and electro-spraying continuously deposited few-micron droplets which may have dried before reaching the current collector. For the filter and transfer method, the solution was vacuum filtered onto a 0.22 micron mixed cellulose ester filter paper, and then the CNT mat was transferred to the current collector by placing the dry filter, CNT-side down, onto the titanium and dissolving the filter with acetone vapor followed by acetone soaks. Finally, in an attempt to remove any remaining filter residue, the transferred electrode is then soaked in dilute nitric acid for a few minutes. The CNT on titanium electrodes were electrochemically characterized using 1 M sulfuric acid electrolyte, a titanium foil counter-electrode, and a silver/silver chloride pellet reference-electrode.

The resulting CNT electrodes were weighed with a Mettler Toledo XP 26 balance, imaged with a Hitatchi S4500 field emission scanning electron microscope (SEM), and electrochemically tested using a Princeton Applied Research VersaStat 3 potentiostat in a three-electrode geometry. Electrochemical characterization consisted of cyclic voltametry (CV) performed at a 20 mV/s scan rate over voltage ranges appropriate to the electrolyte used. The fabrication-method-comparison electrodes on titanium were also characterized with electrochemical impedance spectroscopy (EIS), from 50 mHz to 100 kHz, performed at 0.45 V to avoid any of the redox peaks seen in the cyclic voltamograms.

A single-layer graphene electrode was prepared by chemical vapor deposition of single-layer graphene on a copper catalyst layer and then transferring the graphene to a quartz substrate [11]. An approximately 15 mm internal diameter alumina tube was then glued and clamped to the graphene/quartz sample using Loctite 496 and a polycarbonate fixture (which prevented any mechanical damage to the graphene.) This ceramic tube served as the cell to contain the electrolyte as well as defining the exposed area of graphene. The ends of the graphene extending outside of the ceramic cell were electrically contacted with the aid of silver paint. For these measurements a 1 M sulfuric acid electrolyte was used along with a platinum wire counter electrode and a silver/silver chloride pellet reference electrode. The CV for this electrode was performed over a narrow potential window of −50 mV to −450 mV to avoid any redox peaks. The current to calculate the capacitance was taken as one half the difference between the oxidation and reduction loops at the midpoint of the potential scan range. As usual, the capacitance is then calculated as Capacitance = Current (A)/Scan Rate (V/s).

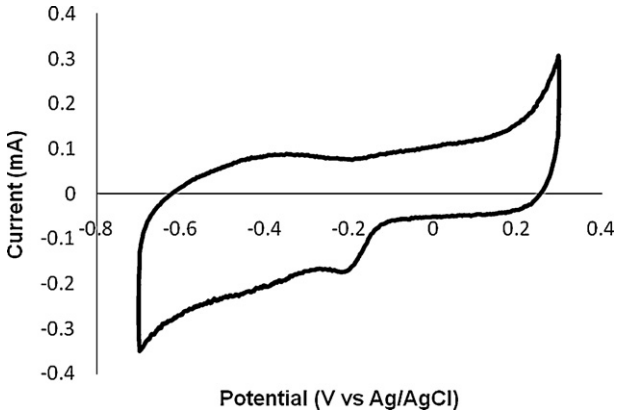

Fig. 1. Typical 20 mV/s cyclic voltammogram for SWCNT electrodes produced using the Brewer Science solution. While there are redox peaks superimposed on the approximately rectangular CV curve that is representative of double layer capacitance, the current for calculating the capacitance is measured on the reduction side (lower curve) at 0.45 V.

3. Results and discussion

Measurement methodologies can contribute to significant differences in measured capacitances. Therefore, standard test conditions of 20 mV/s have been used here for the CV measurements. When characterizing electrochemical capacitors, one needs to be careful to distinguish between double-layer capacitance and any pseudocapacitance contributions. To avoid inclusion of any pseudocapacitive contributions, the capacitance has been calculated for each electrode using the current measured, on the reduction side of the CV loop, at a potential that avoids any redox peaks. In Fig. 1, which is a typical CV, the current was measured on the reduction loop at 0.45 V (vs Ag/AgCl), to avoid the redox peak(s) that appears as the potential is scanned more negatively. This is a much more conservative measurement of capacitance than results from integrating the CV curve or from two electrode measurements which would include the redox contributions. All of the measurements were made at 0.45 V for the electrodes measured in sulfuric acid. Electrochemical impedance spectra were also measured at 0.45 V. In order to compare the capacitances generated by the different fabrication methods, we calculated specific capacitance (F/g) using only the mass of the SWCNTs after subtracting the capacitance of a blank metal foil current collector. Specific capacitances have been calculated from the CV curves using the measured masses of the CNTs as well as masses calculated from the solution concentrations and volumes used. Measured masses more accurately reflect performance when CNTs are lost in processing (e.g., overspray or incomplete filtering). Calculated masses are more accurate when there may be residual contamination that add mass (e.g., incomplete filter paper removal). Specific capacitances from at least three duplicate electrodes have been averaged for reporting for each fabrication method.

3.1. SWCNT solution comparison

CNTs are frequently processed as suspensions/solutions. In order to get stable dispersions, the CNTs are either chemically functionalized and/or dispersed with a surfactant. Both approaches have drawbacks. Chemical functionalization can make the material more soluble, but the addition of these functional groups introduces defects that can decrease conductivity. Functional groups can also be redox active and produce undesirable decomposition byproducts over time. Surfactants can be used in place of functionalization to help increase the solubility of CNTs, but since they are generally nonconductive, they typically degrade performance. Therefore, further processing is required to remove surfactant residues, which may remove CNTs from the substrate or alter the electrode morphology.

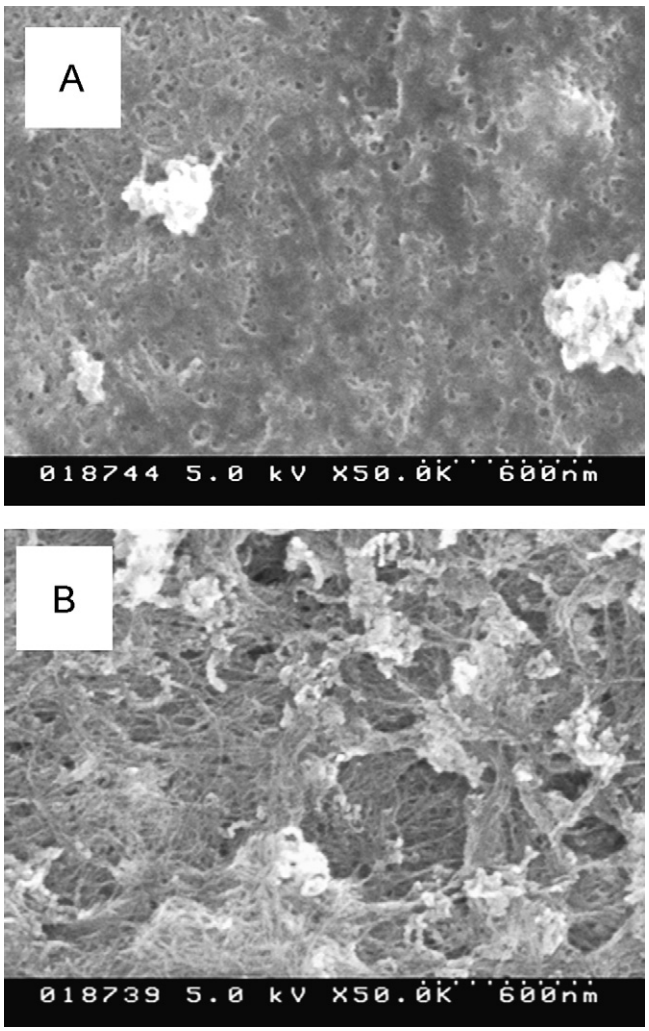

Fig. 2. (A) SWCNT electrode made using a SWCNT solution that included a surfactant. (B) SWCNT electrode made with a surfactant-free solution of SWCNTs resulting in a cleaner and more porous electrode with better electrical conductivity.

In order to investigate the effect of surfactants on the resulting electrodes, we made electrodes from surfactant-free and surfactant-containing CNT solutions made in house. These electrodes were examined in an SEM and greatly reduced porosity was seen when surfactant was used as can be seen in Fig. 2. Electrochemical testing showed the CNT electrode made without surfactants in Fig. 2b has six times the conductivity and four times less contact resistance, when probed with an ohmmeter, as the surfactant containing electrode shown in Fig. 2a. The surfactant-containing electrode resulted in 14 F/g versus 24 F/g for the surfactant-free electrode in this case. While the differences between surfactant-free and surfactant-containing electrodes is highly variable, due in part to how much surfactant is removed by rinsing etc., the surfactant-free electrodes consistently produce better performance, as we have observed in previous work in our lab [12].

Electrodes were also made using the commercial surfactant/dispersant containing SWCNT solutions in acetone. Attempts to remove these additives through thermal annealing, acid washing, or solvent extraction were largely unsuccessful. As a result, these electrodes also had poor capacitances due to low accessible

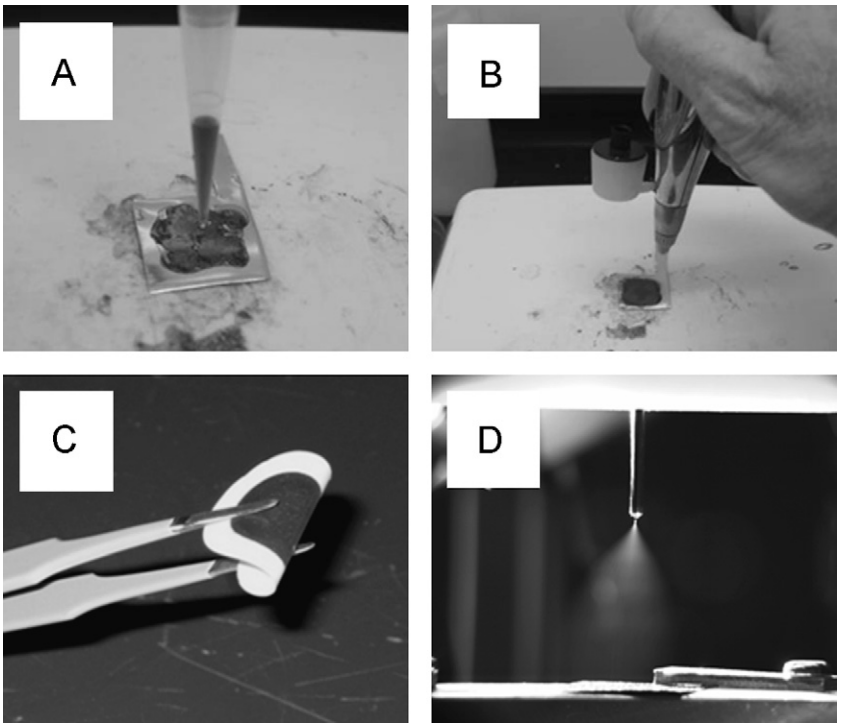

Fig. 3. Pictures of the different deposition methods used (A) drop casting, (B) air brushing, (C) a SWCNT deposit (black) on a mixed cellulose filter paper, and (D) electrospraying.

surface area and high resistivity due to poor tube-to-tube electrical contact.

Subsequent electrodes have been made using the Brewer Science Inc. surfactant-free SWCNT in water solution. This solution yielded much better-looking and higher performing electrodes as will be seen below. While it may be possible to remove surfactant residues depending on the solution used, we have concluded that using surfactant/dispersant-free solutions of SWCNTs is the better approach because it eliminates the need to remove the surfactant altogether. Unfortunately, working with surfactant-free solutions requires the use of lower concentrations.

3.2. Fabrication method comparison

At the outset of this work, it was assumed that the amount of SWCNT bundling would be a significant factor in the capacitance

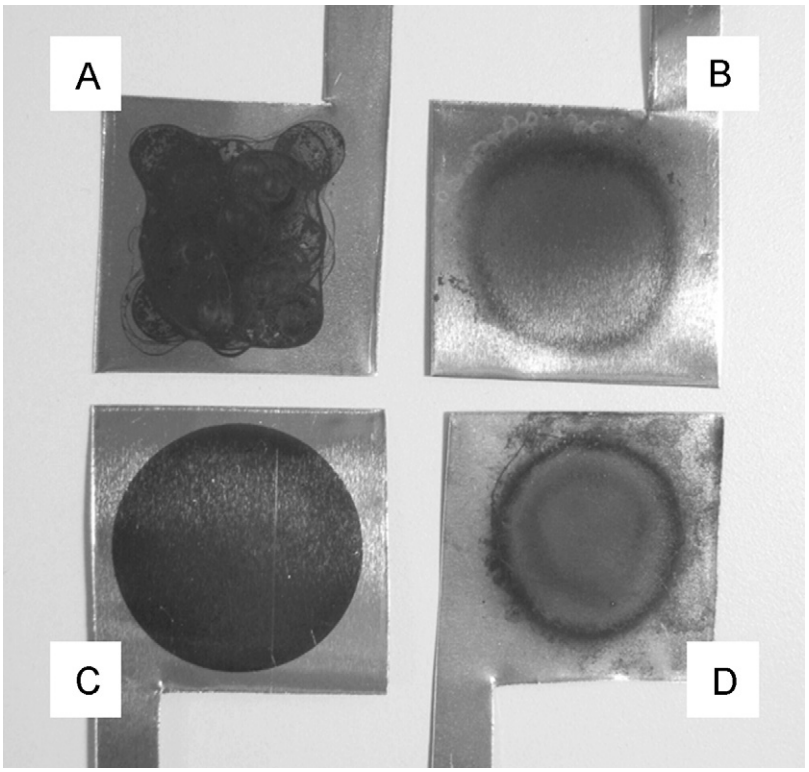

Fig. 4. Photographs of electrodes fabricated using the four methods (A) drop cast, (B) air brushed, (C) filtered/transferred, and (D) electrosprayed.

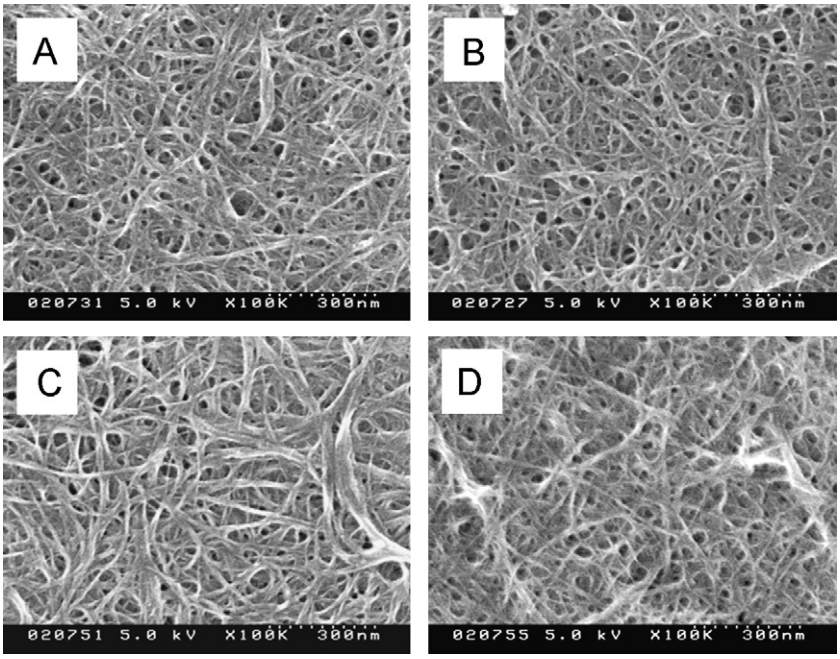

Fig. 5. SEM micrographs of electrodes fabricated using the four methods (A) drop cast, (B) air brushed, (C) filtered/transferred, and (D) electrosprayed.

that could be achieved, and that it may also affect the power performance due to the electrolyte mass transfer resistance to reach the interior bundle surfaces. Therefore, methods for producing solutions of unbundled SWCNTs and deposition methods that prevent re-bundling as the solution dried would be desirable. With this in mind, four methods for depositing the CNT solutions that might yield different amounts of bundling were selected for comparison. By reducing the droplet size, it may be possible to reduce the number of tubes available for bundling during droplet drying, and faster drying times may kinetically limit the bundling.

Drop Casting consists of depositing droplets of solution onto the current collector and evaporating the droplets over 1–2 min, with the total deposition taking about 20 min. Air brushing sprays much smaller droplets onto the current collector; and the droplets dry in 1–3 s with the total deposition time being about 30 min. Vacuum filtration, takes a few seconds total. The last method, electrospraying [13], required a dilution of the solution with ethanol (1:3 v/v CNT/water:ethanol) to decrease surface tension and increase conductivity. Electrospraying produces extremely small droplets, on the order of 4 microns in diameter for pure ethanol, and they may even dry before reaching the current collector. In addition, as the droplets dry in transit, the charge density on the droplets may increase enough that columbic repulsion within the droplets could cause the droplets to explode, perhaps preventing or reducing SWCNT bundling. To ensure that the added ethanol was not responsible for any differences observed with electrospraying, some drop cast electrodes were also made with added ethanol. Pictures of the four deposition methods are shown in Fig. 3.

The resulting electrodes were characterized photographically and through SEM imaging. Fig. 4 contains photographs showing electrodes made with the four different methods. The area that the SWCNTs were deposited over was roughly the same for the four methods. The filtration and transfer method produced the most uniform deposit, while drop casting yielded the most inhomogenous deposit. SEM images of the four electrodes are shown in Fig. 5. At a microscopic scale, the four electrodes look very much the same, with SWCNT bundles on the order of ~5–50 nm in diameter being typical. The filtered electrode bundle distribution appears somewhat skewed to larger bundles sizes, and the electrosprayed electrode appears to have slightly smaller bundles. The microscopic similarity between these electrodes would seem to indicate that the deposition methods investigated have little effect on the resulting electrode topography and therefore capacitance.

Fig. 6 shows the specific capacitances that result from these electrode fabrication methods. These results were calculated using the measured masses of CNTs deposited. It can be seen in Fig. 6 that all of the fabrication methods, except filtration and transfer, yield specific capacitances within two standard deviations (95% confidence) of 35 F/g. It is expected that the filtered and transferred electrodes do not perform as well due to the presence of filter paper residue which increases the measured mass while also likely reducing the capacitance.

When the specific capacitances are recalculated using CNT masses calculated from the solution concentration and volume, as

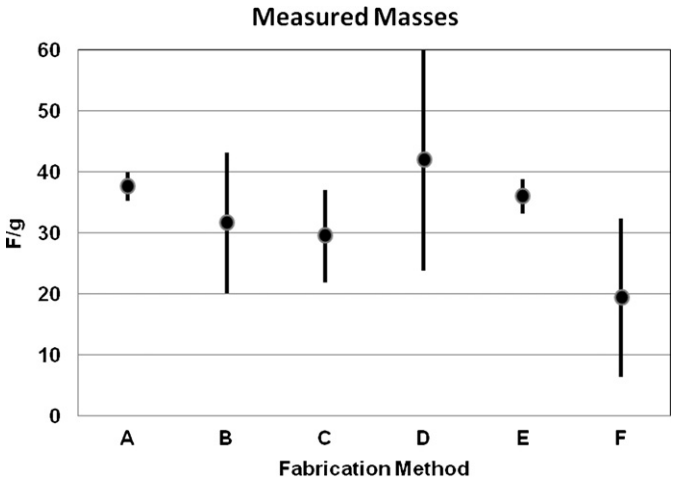

Fig. 6. Plot of specific capacitances achieved with the various fabrication methods when the CNT mass is measured with a balance. Fabrication methods: (A) drop cast – no sonication, (B) drop cast – sonicated neat, (C) drop cast – sonicated with ethanol, (D) electrosprayed – sonicated with ethanol, (E) airbrushed – sonicated neat, and (F) filtered and transferred – neat without sonication.

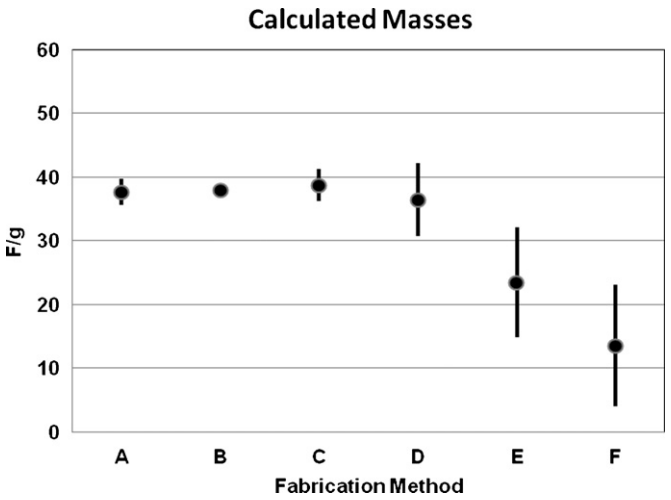

Fig. 7. Plot of specific capacitances achieved with the various fabrication methods when the CNT mass is calculted from the volume and concentration of the deposited CNT solution. Fabrication methods: (A) drop cast – no sonication, (B) drop cast – sonicated neat, (C) drop cast – sonicated with ethanol, (D) electrosprayed – sonicated with ethanol, (E) airbrushed – sonicated neat, and (F) filtered and transferred – neat without sonication.

shown in Fig. 7, one can see that the drop cast and electrosprayed electrodes have virtually identical performances. In this case, the airbrushed and filtered electrodes do not compare well due to CNT loss during deposition. During airbrushing some droplets may miss the titanium altogether or be blown off before they dry as reflected in lower measured masses than predicted. In filtration, CNTs are visibly present in the filtrate. In both cases the CNT mass calculated from the solution concentration is an overestimate of the actual mass of CNTs deposited. In Fig. 7, it can also be seen that sonication with or without added ethanol has not affected the electrode performance.

The EIS characterization, of all of the electrodes fabricated, did not show significant qualitative differences between the electrodes. Fig. 8 shows the typical EIS results from a drop cast electrode. The Nyquist plot shown in Fig. 8a shows a small RC loop at high frequency. This is likely due to a surface oxide on the titanium current collector since they were only degreased and not etched prior to CNT deposition. Fig. 8b shows a plot of capacitance as a function of frequency. This electrode had a corresponding 45 degree phase angle at 50 Hz. The capacitance retention as a function of cycle number for the electrode is show in Fig. 8c where 94% of the initial capacitance is retained after 1200 cycles.

3.3. Single layer graphene electrode

In Figs. 6 and 7, little difference in specific capacitances based on fabrication method is seen (except when contamination is present) which suggests that the fabrication methods investigated here have not significantly affected the amount of CNT bundling. While bundling might be beneficial for increasing the electrical conductivity of the CNT electrode, it has been assumed here that it is detrimental due to a reduction of the accessible surface area of the electrode. However, this may not be the case. It has been reported that CNT electrodes expand and shrink during cycling which could be indicative of at least partial debundling [14]. The bundle expansion may be due to electrostatic repulsion between like charged CNTs or due to oppositely charged electrolyte ions forcing their way in between the CNTs. Therefore the question becomes what is the highest specific capacitance that could be achieved if the entire CNT surface area was readily accessible? Have we already achieved

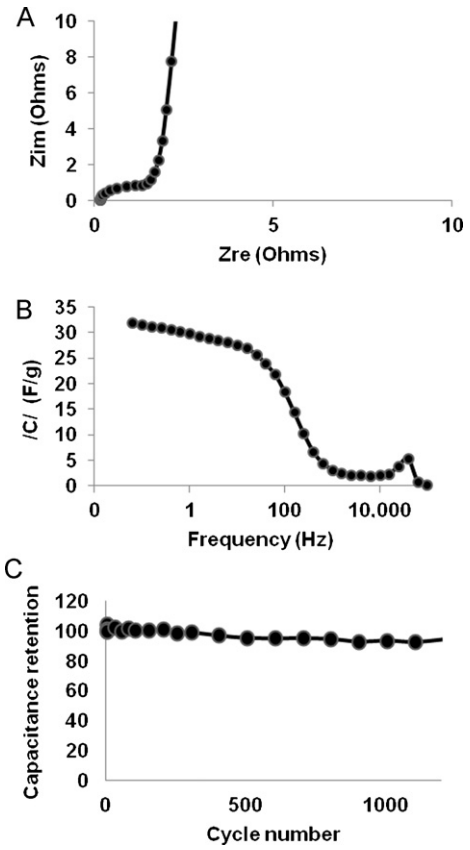

Fig. 8. EIS and capacitance retention testing of a typical drop cast CNT electrode. (A) Nyquist plot, (B) capacitance as a function of measurment frequency, and (C) capacitance retention over 1200 cycles.

the maximum possible specific capacitance for CNTs or is further optimization warranted?

In an attempt to answer these questions, a model system of a single-layer graphene electrode on sapphire was tested. This should be a reasonable model for single-wall CNTs since the electrolyte can only access one side of the graphene (corresponding to the outside of a SWCNT). Fig. 9 shows the 20 mV/s CV of the single-layer graphene electrode. The CV curve is seen to be somewhat distorted due to the high resistance in the electrode. The graphene was electrically contacted at both sides and a resistance from one lead to the other of 4.3 kΩ was measured. This resistance is a combination of contact resistance between the silver paint and the graphene, as well as the resistance of the graphene itself. In addition, in this potential region, there is a redox current due to the reduction of

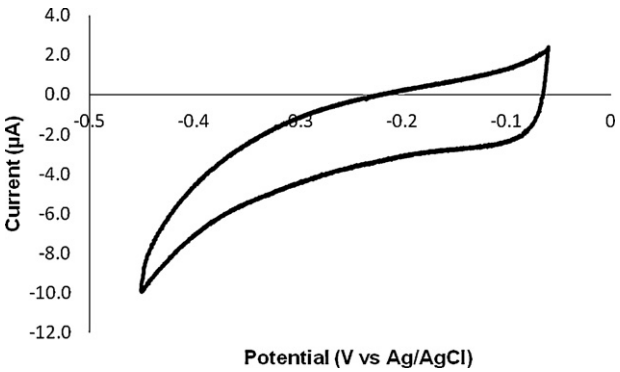

Fig. 9. CV of single-layer graphene on saphire electrode taken at 20 mV/s using 1 M sulfuric acid electrolyte and a silver/silver chloride pellet reference electrode.

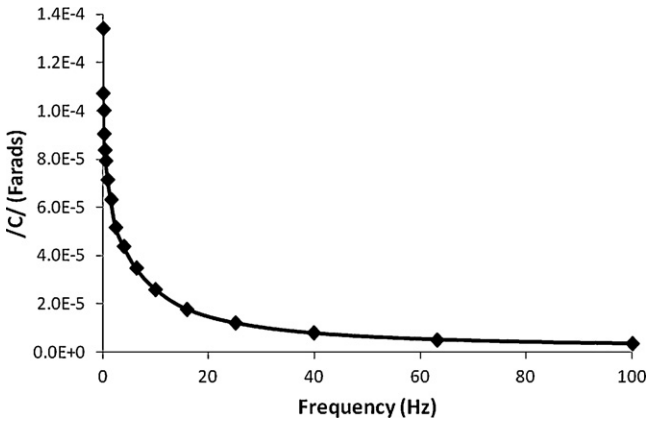

Fig. 10. EIS measurement of capacitance versus frequency for a large-area single-layer graphene electrode.

oxygen since the measurements were performed in an open cell. This oxygen reduction current is expected to be diffusion limited and so is expected to shift the CV curve towards negative currents but not affect the area within the CV curve which represents the capacitance. The measured capacitance of 42 $\mu F/cm^2$ is very close to the expected intrinsic capacitance of one molar sulfuric acid [15]. At 76 ng/cm^2 for graphene (only counting one side of the graphene towards the surface area), this corresponds to 550 F/g that should be achievable with SWCNTs. This is, at this time, only an estimate for the specific capacitance of graphene. If the CV measurement is made a lower scan rate (e.g. 5 mV/s) a higher capacitance is measured (although measurement errors get more significant at lower scan rates). The EIS measurement (Fig. 10) shows that our CV measurements fall on a steep slope in the capacitance versus frequency curve indicating that these results should be interpreted with some caution (20 mV/s corresponds to approximately 0.75 Hz in this EIS measurement). Unfortunately, the curve is not seen to plateau at the lower frequencies (which would yield the true capacitance limit) due to the large time constant that results from the large resistance of the single-layer graphene electrode. Attempts to improve this measurement to obtain the true capacitance of single-layer graphene are on-going. However, if single sided graphene is a suitable model for SWCNTs, it is already clear from these results that we are not reaching the potential of SWCNT electrodes with the current fabrication methods, presumably due to CNT bundling or insufficient porosity resulting in reduced electrolyte accessible surface area.

4. Conclusions

A systematic comparison of different CNT solution compositions and deposition methods has been undertaken to determine the important factors in electrode fabrication. We have found that it is best to use CNT solutions free from additives that may be difficult to remove from the fabricated electrode. The CNT solution composition and processing is more important than the choice of the CNT deposition methods used here. In the end, the choice of fabrication method may be determined by other factors such as manufacturability or the efficiency with which the SWCNTs are used.

Since the achieved specific capacitances are not approaching the capacitance predicted with a single-layer graphene electrode, more work needs to be done to develop an optimized CNT electrode. Since the differences between the fabrication methods used here are not large, other approaches to optimizing the electrodes, such as using double- or multiple-wall tubes (which result in less bundling and larger pores) and the incorporation of functional groups or nanoparticles to induce spacing between the CNTs should be investigated.

Even if CNTs electrodes do not yield specific capacitances in excess of activated carbon, they may still yield improvements in power due to increased electrode conductance and optimized porosity. There may also be important electrochemical capacitor improvements due to the mechanical properties of CNTs. For instance, CNTs may lend themselves to flexible, conformal, or integrated electrochemical capacitors that would be useful for applications where there is little available space.

References

[1] A.G. Pandolfo, A.F. Hollenkamp, J. Power Sources 157 (2006) 11–27.
[2] X. Zhao, Nanotechnology 20 (2009) 065605.
[3] M. Kaempgen, et al., Nano Lett. 9 (2009) 1872–1876.
[4] S.W. Lee, et al., J. Am. Chem. Soc. 131 (2009) 671–679.
[5] L. Cooper, et al., Appl. Phys. Lett. 95 (2009) 233104.
[6] S.-L. Chou, et al., Electrochem. Commun. 10 (2008) 1724–1727.
[7] J.H. Kim, K.-W. Nam, S.B. Ma, K.B. Kim, Carbon 44 (2006) 1963–1968.
[8] L. Hu, et al., Proc. Natl. Acad. Sci. U.S.A. 106 (2009) 21490–21494.
[9] J. Wang, M.W. Ellsworth, Electrochem. Soc. Trans. 19 (2009) 241–247.
[10] M. Stoller, R. Ruoff, Energy Environ. Sci. 3 (2010) 1294–1301.
[11] X. Li, et al., Nano Lett. 9 (2009) 4359–4363.
[12] C.M. Anton, M.H. Ervin, Electrochem. Soc. Trans. 33 (2011) 117–128.
[13] A.J. Jaworek, Mater. Sci. 42 (2007) 266–297.
[14] P.W. Ruch, R. Kotz, A. Wokaun, Electrochim. Acta 54 (2009) 4451–4458.
[15] R. Istvan, The 20th International Seminar on Double Layer Capacitors & Hybrid Energy Storage Devices, Deerfield Beach, FL, December 6–8, 2010, 2010.