



## **SWCNT Supercapacitor Electrode Fabrication Methods**

**by Matthew H. Ervin, Benjamin S. Miller, and Brendan Hanrahan**

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**Matthew H. Ervin, Benjamin S. Miller, and Brendan Hanrahan**  
**Sensors and Electron Devices Directorate, ARL**

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| 14. ABSTRACT<br><p>This work systematically compares various solution-based electrode fabrication methods (drop casting, air brushing, filtration, and electrospraying) to determine if there is an optimum method for fabricating supercapacitor electrodes out of single-wall carbon nanotubes (SWCNT). We have found that it is best to use SWCNT solutions free from additives that may be difficult to remove from the fabricated electrode. In addition, the SWCNT solution processing (e.g., dilution and sonication) has a small effect on the resulting specific capacitance, as did the deposition methods compared here.</p>                                                                                                                                                                                                                                                                                                                             |                             |                              |                                         |                                                                |                                                             |
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## 1. Background

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Supercapacitors, more properly referred to as electrochemical capacitors, have several advantages over conventional batteries, including higher specific power ( $\sim 2$  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). Increasing supercapacitor energy and power densities will make them more useful for portable power applications.

A supercapacitor 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 redox reactions at the electrodes, whose rates are potential dependent. This type of energy storage is referred to as pseudocapacitance since it behaves as a capacitance, though the charge transfer reactions are more like that of a battery. Since there is no dielectric on the supercapacitor electrodes, the applied biases must remain low enough that electrochemical breakdown of the electrolyte solvent or charge transfer between the ions and electrodes (except when pseudocapacitance is desired) do not occur. This limits the voltage rating on individual supercapacitor cells to about 1.2 V when using aqueous electrolytes, and 3.5 V when using organic electrolytes.

Supercapacitors 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 supercapacitors. Two materials being studied for this are carbon nanotubes (CNTs) and graphene. Graphene is a single atomic layer of graphite. Similarly, a single-wall CNT (SWCNT) is a single atomic layer of graphite that curve back on itself to form a tube. Multi-wall carbon nanotubes (MWCNTs) are carbon nanotubes that are more than one atomic layer thick; 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.

This report details investigations into various solution-based electrode fabrication methods that are compared to determine if there is an optimum method for fabricating SWCNT electrodes. Solution-based processing was chosen, as it is manufacturable and does not impose significant thermal and chemical constraints on the underlying current collector as direct growth on the current collector 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 solution-based processing approaches have been demonstrated with measured specific capacitances of 23–200 F/g, as shown by the representative works listed in table 1 (2–9). Since these papers use different CNT sources, solution compositions/processing, deposition methods, and characterization protocols, it is difficult to draw meaningful conclusions about the electrode fabrication methods from a comparison of these works. In addition, many of the higher specific capacitances, reported in table 1, likely include pseudocapacitive contributions to the measured specific capacitance. Such pseudocapacitance contributions may overwhelm the double-layer capacitance, which is the focus of this work, as the double-layer capacitance is related to the realized accessible electrode surface area. Here we have systematically investigated the individual contributions of the solution preparation and the deposition methods to achieved double-layer capacitance.

Table 1. Examples of solution processed CNT/graphene electrodes.

| <b>Fabrication method</b>   | <b>CNT solution</b>                 | <b>F/g</b> | <b>Comments</b>                                                            | <b>Reference</b>              |
|-----------------------------|-------------------------------------|------------|----------------------------------------------------------------------------|-------------------------------|
| Spray Deposition            | SWCNT                               | 38         | SWCNTs not functionalized                                                  | X Zhao Nanotech 2009 (2)      |
| Spray Deposition            | SWCNT-COOH                          | 155        | Functionalization results in clear redox pseudocapacitance                 | X Zhao Nanotech 2009(2)       |
| Spray Deposition            | MWCNT                               | 23         | MWCNTs not functionalized                                                  | X Zhao Nanotech 2009(2)       |
| Spray Deposition            | MWCNT-COOH                          | 77         | Functionalization results in clear redox pseudocapacitance                 | X Zhao Nanotech 2009(2)       |
| Spray Deposition            | SWCNT                               | 90–120     | SWCNTs possibly functionalized during purification                         | Kaempgen NL 09 (3)            |
| Layer by Layer              | MWCNT-COOH<br>MWCNT-NH <sub>2</sub> | 150        | Pseudocapacitance contribution                                             | S W Lee JACS 08 (4)           |
| Filtration                  | DWCNT                               | 67         | DNA dispersed double walled CNTs                                           | Cooper APL 2009 (5)           |
| Filtration                  | DWCNT                               | 32         | Double walled CNTs                                                         | Chou Electrochem Comms 08 (6) |
| Electrospray                | MWCNT-COOH                          | 108        | Pseudocapacitance contribution                                             | J H Kim Carbon 06 (7)         |
| Meyer Rod - Adsorb on Paper | SWCNT                               | 200        | Measurements indicate at least some pseudocapacitance                      | Hu PNAS 09 (8)                |
| Freeze Dry                  | graphene                            | 120        | 200 °C anneal of graphene oxide may not remove all oxide functional groups | J. Wang ECS Trans. 09 (9)     |

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## 2. Capacitor Evaluation

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When characterizing capacitors, one needs to be careful to distinguish between double-layer capacitance and any pseudocapacitance contributions. In addition, measurement methodologies can contribute to significant differences in measured capacitances. Therefore, standard test conditions of 20 mV/s have been used for cyclic voltametry (CV) measurements made using one molar potassium hydroxide (KOH) electrolyte. To avoid inclusion of any reduction and oxidation (redox) (pseudocapacitive) contributions, the capacitance has been calculated for each electrode using the current measured at the open circuit potential on the reduction side of the CV loop. In figure 1, this would correspond to measuring the CV current on the lower portion of the curve at approximately  $-0.1$  V, which avoids the redox peak(s) that starts at about  $-0.2$  V as the potential is scanned more negatively. At the open circuit potential, any redox reactions should be in equilibrium and make no contribution to the measured current. Electrochemical impedance spectroscopy was also performed at the open circuit potential. 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 the metal foil current collector. It became apparent during the experiments that there was excessive error in the measured SWCNT masses. This error was tracked down to magnetic field effects while measuring our nickel current collector-based electrodes. Therefore, the reported results will rely on masses calculated from the solution concentrations/volumes used. Since this is not wholly accurate, due to mass loss from overspray or incomplete filtering, some experiments have been repeated using nonmagnetic tungsten current collectors in order to verify the trends.

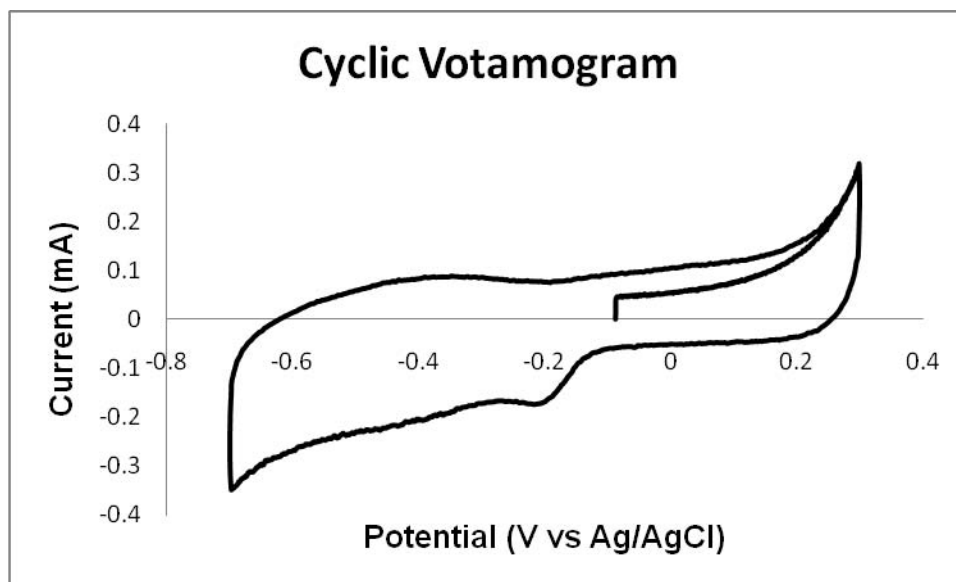


Figure 1. Typical 20 mV/s cyclic voltammogram for SWCNT electrodes produced in this study. While there are redox peaks superimposed on the approximately rectangular CV curve that is representative of double layer capacitance, the current for calculating the capacitance is measure on the reduction side (lower curve) at the open circuit potential which is at  $-88$  mV in this example.

### 3. SWCNT Solution Comparison

Both SWCNT and graphene materials are frequently processed as suspensions/solutions. In order to get stable dispersions, the SWCNTs/graphene 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 solubilize SWCNTs or graphene, but since they are generally nonconductive, they typically degrade performance. Therefore, further processing is required to wash them off, which may remove SWCNTs/graphene from the substrate or alter the electrode morphology. We have made numerous electrodes using SWCNT solutions obtained from commercial sources. The first solutions used were of functionalized or unfunctionalized SWCNTs suspended in acetone, using surfactants and/or dispersants containing:  $\alpha$ -(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 electrodes were examined in a scanning electron microscope (SEM) and little porosity was seen. The anticipated porosity between the SWCNTs was filled with surfactant/dispersant additives, as is shown in figure 2a. Attempts to remove these additives through thermal

annealing, acid washing, or solvent extraction were largely unsuccessful. As a result, the electrodes had poor capacitances due to low accessible surface area and high resistivity due to poor tube-to-tube electrical contact.

Subsequent electrodes were made using SWCNTs functionalized with carboxyl groups by refluxing in strong acids. These SWCNTs are somewhat soluble in water without the aid of surfactants/dispersants, and they yield much better-looking (figure 2b) and higher performing electrodes. The SWCNT mat made without surfactants in figure 2b has six times the conductivity and four times less contact resistance, when probed with an ohmmeter, as the surfactant containing mat shown in figure 2a. While the differences in conductivity between surfactant-free and surfactant-containing mats is highly variable, the surfactant-free mats consistently produce better properties, as we have observed in other work in our lab (10). We concluded that using surfactant/dispersant free solutions of SWCNTs is the better approach, even though it requires the use of less concentrated solutions.

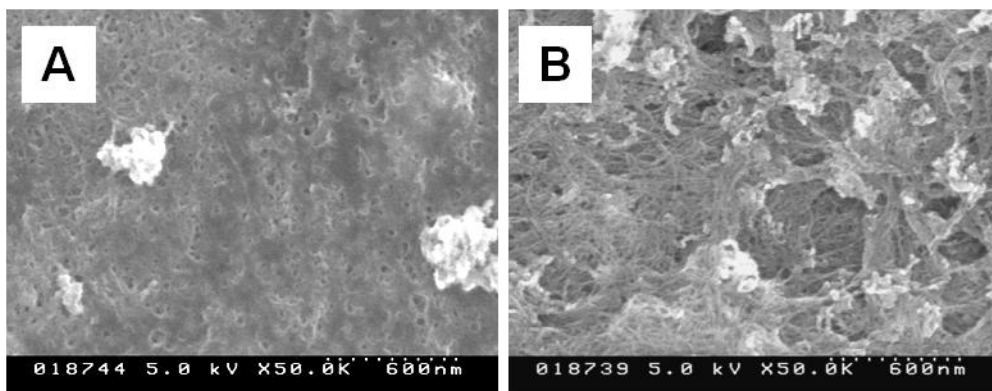


Figure 2. (a) SWCNT electrode made using a SWCNT solution that included a surfactant (b) SWCNT electrode made with a surfactant-free solution of SWCNTs resulting in a cleaner and more porous electrode with better electrical conductivity.

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## 4. Fabrication Method Comparison

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At the outset of this work, it was assumed that the amount of SWCNT bundling would be a significant factor in the capacitance that could be achieved. It may also affect the power performance due to the electrolyte resistance to reach the interior electrode surfaces. Therefore, methods for producing solutions of unbundled SWCNTs and deposition methods that prevent re-bundling as the solution dried would be critical. In light of this, four methods for depositing the SWCNT solutions that might yield different amounts of re-bundling were selected for comparison. All four methods were used to deposit 1ml of SWCNT solution of  $\sim 70$   $\mu\text{g}/\text{ml}$  water concentration onto nickel current collectors, which were heated on a  $175^\circ\text{C}$  hot plate during the deposition (except for the filter and transfer method).

The easiest method, 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. The second method, air brushing, sprays much smaller droplets onto the current collector; the droplets dry in 1–3 s, with the total deposition time being about 30 min. The third method, vacuum filtration, takes a few seconds total, and is followed by transferring the dry SWCNT mat to the current collector by placing the filter face down onto the current collector and dissolving the mixed cellulose filter (0.22 micron) with acetone. The last method investigated is electrospraying (11), which required a dilution of the solution with ethanol (1:0.43 v/v water:ethanol) to decrease its surface tension. This method produces extremely small droplets, on the order of 4 microns in diameter, and they may 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 cause the droplets to explode, perhaps preventing or reducing SWCNT bundling. Pictures of the four deposition methods are shown in figure 3.

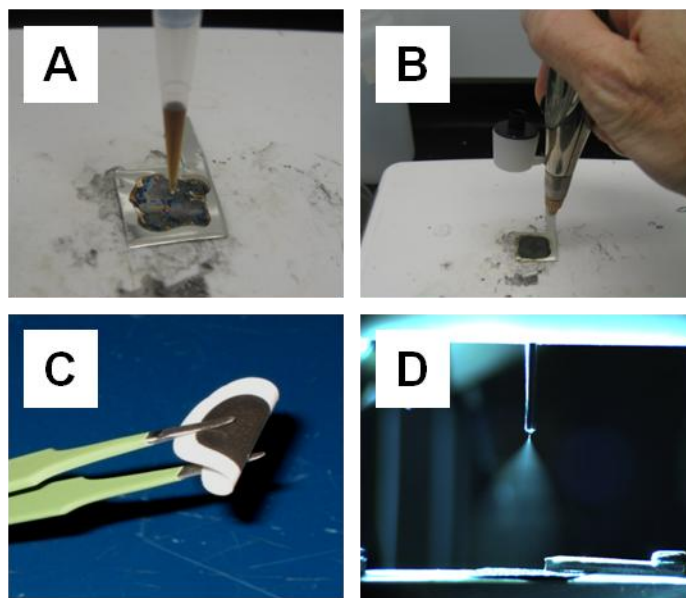


Figure 3. Pictures of the different deposition methods used (a) drop casting, (b) air brushing, (c) a SWCNT deposit (black) on a mixed cellulose filter paper, and (d) electrospraying.

The resulting electrodes were characterized photographically and through SEM imaging. Figure 4 is a photograph 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 non-homogenous deposit. SEM images of the four electrodes are shown in figure 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, and with the filtered electrode distribution, perhaps, being skewed somewhat to the larger bundles and the electrosprayed electrode to the smaller

bundles. The microscopic similarity between these electrodes would seem to indicate that the deposition methods investigated are having little effect on the resulting electrode topography.

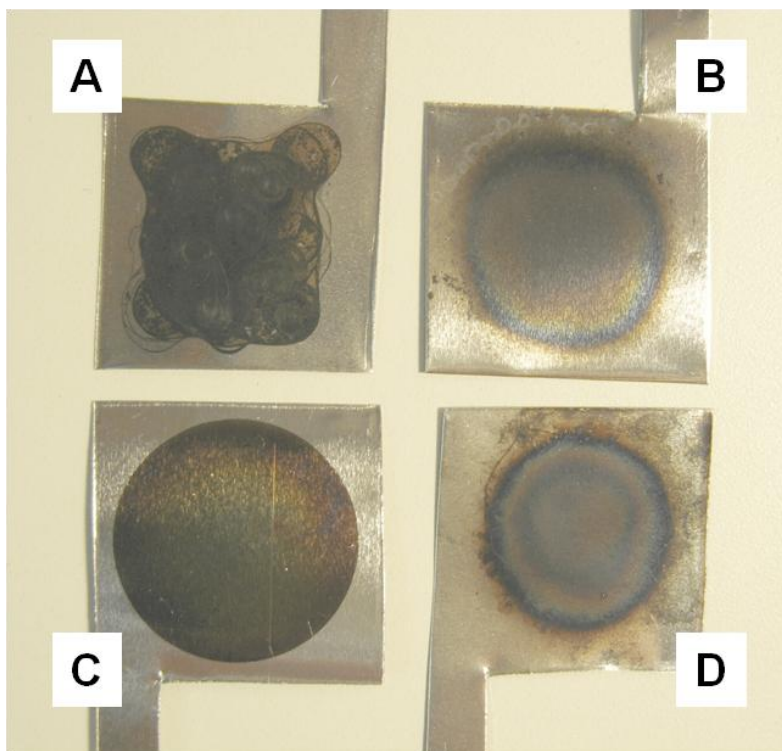


Figure 4. Photographs of electrodes fabricated using the four methods (a) drop cast, (b) air brushed, (c) filtered/transferred, and (d) electrosprayed.

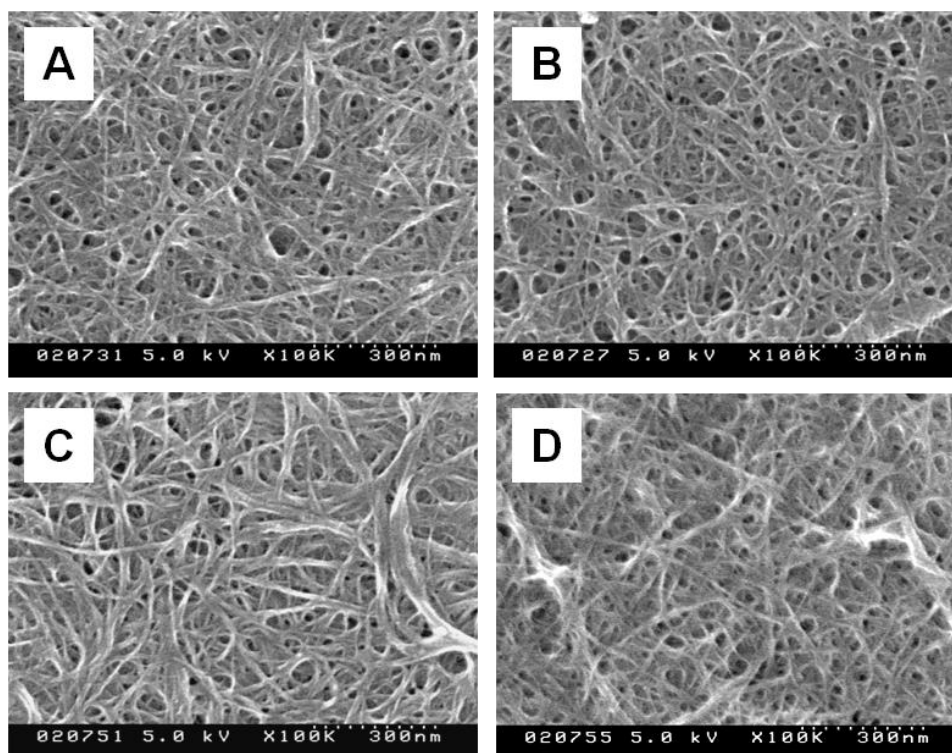


Figure 5. SEM micrographs of electrodes fabricated using the four methods (a) drop cast, (b) air brushed, (c) filtered/transferred, and (d) electrosprayed.

Figure 6 shows the specific capacitances that result from these electrode fabrication methods. Focusing on the diamond symbols in the graph, which are electrodes generated with the solution used as is, it appears that these different methods do not result in greatly different capacitances. In fact, the differences may be less than they appear since the lower specific capacitances of the air-brushed, filtered, and, perhaps, electrosprayed methods may be due in part to a loss of SWCNTs due to overspray, or incomplete filtration of the SWCNTs. (Remember that the SWCNT masses were calculated from the solution used and not measured due to difficulty in getting accurate masses at the tens of microgram level used here.) The “x” symbols in the figure represent electrodes made from SWCNT solutions sonicated with added ethanol, water, or no added solvent. Again, it appears that the SWCNT solution preparation (sonication and dilution with ethanol) may be at least as significant as the fabrication methods used here.

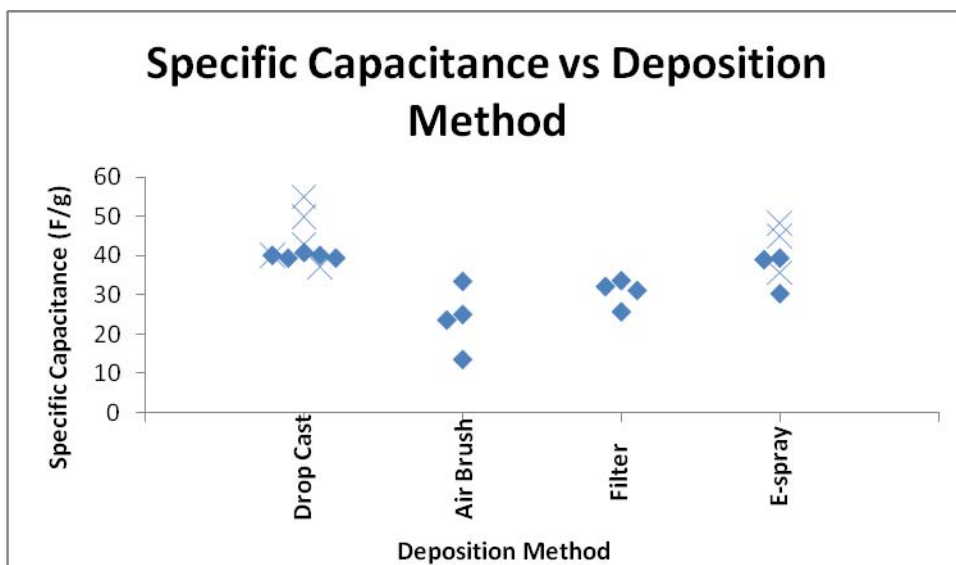


Figure 6. Specific capacitance as a function of deposition method. The diamonds are from samples made with the SWCNT solution merely shaken, while the “x” symbols are used to denote samples made from sonicated SWCNT solutions.

In order to investigate whether the lower specific capacitances resulting from air brushing and filtering were due to loss of SWCNTs during the deposition, two more electrodes were made. One was air-brushed onto a current collector with upturned edges to minimize the amount of SWCNT solution droplets that were blown off the substrate during deposition. This electrode clearly showed an additional deposit of SWCNTs at the bent up edges of the current collector. The other was made by triple-filtering the SWCNT solution through the same filter paper prior to transferring the SWCNTs onto the current collector. In both cases, the more carefully prepared electrodes reproduce the highest specific capacitances seen for those methods in figure 6.

The electrochemical impedance spectroscopic characterization, of all of the electrodes fabricated, did not show significant qualitative differences between the electrodes. However, the one difference that we noticed was that the air-brushed electrodes retained more of their initial capacitance at higher frequencies. Since these electrodes started with lower capacitance and, therefore, likely contain fewer SWCNTs, it would appear that they are thinner electrodes, which could explain why they perform slightly better at higher frequencies. More work would be required to determine if these frequency response differences are significant.

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## 5. Conclusions and Opportunities

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In the present work, a systematic comparison of different SWCNT 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 SWCNT solutions free from additives that may

be difficult to remove from the fabricated electrode. The SWCNT solution composition and processing (e.g., sonication or dilution) are more important than the choice of the SWCNT 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.

Continuing work will focus on the fundamental capacitance limits of SWCNTs/graphene electrodes to determine if further fabrication method development is warranted. We are currently attempting to address this issue by investigating the capacitance achievable with well-defined single-layer graphene electrodes.

Even if SWCNTs/graphene 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 supercapacitor improvements due to the mechanical properties of SWCNTs/graphene. For instance, SWCNTs/graphene may lend themselves to flexible, conformal, or integrated supercapacitors that would be useful for applications where there is little available space.

While the different electrode fabrication methods investigated here appear to yield similar capacitances, the SEM images appear to show potential differences in bundle size distributions. In the end, there may be an optimum bundle size that is small enough to allow easy electrolyte penetration and large enough to enhance conductivity.

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## List of Symbols, Abbreviations, and Acronyms

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|        |                              |
|--------|------------------------------|
| CNTs   | carbon nanotubes             |
| CV     | cyclic voltametry            |
| KOH    | potassium hydroxide          |
| MWCNTs | Multi-wall carbon nanotubes  |
| Redox  | reduction and oxidation      |
| SEM    | scanning electron microscope |
| SWCNT  | single-wall CNT              |

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| 1                | US ARMY INFO SYS ENGRG CMND<br>ATTN AMSEL IE TD A RIVERA<br>FT HUACHUCA AZ 85613-5300                                                                                                                    |
| 1                | COMMANDER<br>US ARMY RDECOM<br>ATTN AMSRD AMR<br>W C MCCORKLE<br>5400 FOWLER RD<br>REDSTONE ARSENAL AL 35898-5000                                                                                        |
| 1                | US GOVERNMENT PRINT OFF<br>DEPOSITORY RECEIVING SECTION<br>ATTN MAIL STOP IDAD J TATE<br>732 NORTH CAPITOL ST NW<br>WASHINGTON DC 20402                                                                  |
| 1                | US ARMY RSRCH LAB<br>ATTN RDRL CIM G T LANDFRIED<br>BLDG 4600<br>ABERDEEN PROVING GROUND MD<br>21005-5066                                                                                                |

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TOTAL: 25 (2 ELEC, 1 CD, 22 HCS)

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