Carbon Nanotubes

Research Summary

Carbon-Nanotube-Based Electrochemical Double-Layer Capacitor Technologies for Spaceflight Applications


Electrochemical double-layer capacitors, or supercapacitors, have tremendous potential as high-power energy sources for use in low-weight hybrid systems for space exploration. Electrodes based on single-wall carbon nanotubes (SWCNTs) offer exceptional power and energy performance due to the high surface area, high conductivity, and the ability to functionalize the SWCNTs to optimize capacitor properties. This paper will report on the preparation of electrochemical capacitors incorporating SWCNT electrodes and their performance compared with existing commercial technology. Preliminary results indicate that substantial increases in power and energy density are possible. The effects of nanotube growth and processing methods on electrochemical capacitor performance is also presented. The compatibility of different SWCNTs and electrolytes was studied by varying the type of electrolyte ions that accumulate on the high-surface-area electrodes.

INTRODUCTION

Energy storage devices are classified according to energy and power density. Power density is related to the strength of a given current and voltage combination (wattage), while energy density is related to the duration of time that wattage can be applied. Electrochemical double-layer capacitors, commonly called supercapacitors or ultracapacitors, are intermediate systems that bridge the power/energy gap between traditional dielectric capacitors (high power) and batteries (high energy).

Batteries are currently the most common form of electrical energy storage. They are typically able to store higher energy density than supercapacitors, but they deliver less power compared to traditional dielectric capacitors. However, due to their short cycle life and low power densities (i.e., <0.1 kW/kg), batteries are not suitable for many lightweight power source applications. Yet, the high energy density present in batteries allows for energy storage over a longer time period. Energy density for non-rechargeable, dry batteries ranges from 90 Wh/kg to 455 Wh/kg. Rechargeable Ni-Cd batteries can achieve 1,000 cycles in a lifetime, with an energy density of approximately 225 Wh/kg.

Conventional capacitors traditionally have much higher power densities than batteries, ranging from $1.0 \times 10^2$ kW/kg to $2.7 \times 10^{10}$ kW/kg. Conventional capacitors also have extended life cycles (i.e., >10,000). However, the small energy density (i.e., <0.05 Wh/kg) of capacitors is a significant drawback for many applications that require a large amount of energy storage or delivery.
Electrochemical double-layer supercapacitors have properties ranging in between these two common energy storage devices. Supercapacitors offer high power density, high energy density, and long cycle life. In addition, conventional capacitors are limited by dielectric breakdown. Dielectric materials that are necessary for traditional capacitors are not needed for supercapacitors. However, supercapacitors typically contain organic electrolytes that may limit their use in some applications. As energy storage devices, supercapacitors could be applied to many emerging technologies such as electric vehicles, satellite propulsion, and pulse power applications.

Supercapacitors incorporating carbon nanotubes (CNTs) can potentially store higher energy density than traditional capacitors with an equivalent amount of delivered power (Figure 1). This property makes them suitable for certain applications (like drills and in-situ resource utilization systems) envisioned for use in human spaceflight to the moon, Mars, and beyond as part of NASA’s “Vision for Space Exploration.”

Three main classes of supercapacitors are described in the literature: metal oxide, electronically conducting polymer, and carbon-based. Recently, hybrid supercapacitors have been

## EXPERIMENTAL PROCEDURES

### Laboratory-Scale SWCNT-Based Supercapacitors

Specially treated aluminum foil sheets supplied by Maxwell Technologies were sectioned into squares measuring 5 cm × 5 cm to serve as the current collector for the laboratory-scale supercapacitor samples. A 5 cm square of Celgard™ was sectioned to serve as the separator material. The active electrode material for the supercapacitor electrode consists of a well-mixed paste made from carboxymethylcellulose (CMC), water, methanol, and single-wall carbon nanotubes (SWCNTs). To gauge the potential for performance differences between manufacturers, two separate SWCNT suppliers were used: HiPco™ SWCNTs from Carbon Nanotechnologies, Inc. and Elicarb™ SWCNTs from Swan Chemical Company.

Six different electrolytes were used in the project: benzylidimethylpropylammonium aluminum tetrachlorate, benzylidimethyl ammonium imide, dimethylammonium imide, ethyldimethyl ammonium bisulfate, 1-butyl-3-methylimidazolium tetrafluoroborate, and tetraethylammonium tetrafluoroborate in acetonitrile. The first five of these electrolytes (Figure A) are termed “room-temperature ionic liquids” and are a new family of chemical compounds useful for electrochemistry applications.

The active electrode material (i.e., the SWCNT-containing paste) is applied in a uniform layer across the two aluminum foil current collectors and the paste is then saturated with a specific electrolyte. The Celgard separator is sandwiched between the two active electrodes and the entire assembly is sealed using kapton tape (Figure B).

Once manufactured, the supercapacitors were subjected to a series of electrical tests and compared to a 10 F commercially available supercapacitor (Maxwell Technologies Model #PC10). Since the academic-scale kapton tape sealing method does not produce nor retain the desired internal pressure that a traditional commercial-scale supercapacitor manufacturing method could generate, a hydraulic press was used during the laboratory electrical testing. The pressure between the two plates of this press (with the supercapacitor in between) is maintained at 6.9 MPa throughout the testing regimen. The primary data reported for the laboratory scale samples are results from a constant voltage test. During this analysis, a voltage of 1.5 V is manually applied via alligator clips attached across the “tabs” of the supercapacitor (Figure B) for between four and five seconds and then instantaneously reduced to zero and held at zero for between four and five seconds while the current is measured. This cycle is then repeated.

### Electrical Testing and Materials Characterization at Johnson Space Center

Three experimental supercapacitors with the highest reported performance during initial testing at Georgia Tech Research Institute, in addition to a Maxwell PC10 10 F supercapacitor, were submitted for further testing at NASA Johnson Space Center. A standard constant current charge/discharge cycle was chosen to characterize capacitance and equivalent series resistance of the capacitors. A tensile tester with a 4,536 kg load cell was used to apply the recommended 6.9 MPa of pressure. For the sake of completeness, loads from 0 kg to 1,361 kg were also applied. The supercapacitor leads were connected to a direct-current power supply with voltage limited to 1.5 V and current set at 20 mA or 50 mA (200 mA in the case of the Maxwell PC10). The capacitor was charged for a fixed time, 8 s to 12 s, while voltage was measured. The charge current was removed and the capacitor was then discharged before repeating the test. Voltage was recorded for the charge portion of the cycle only.

![Figure A. A schematic diagram and chemical name for room-temperature ionic liquid (RTILs) used in laboratory-scale supercapacitor manufacture. The number to the left of the structure indicates the nomenclature used to designate each RTIL throughout this effort.](image1.png)

![Figure B. A schematic diagram (left) and laboratory-scale supercapacitor (right).](image2.png)
developed where an activated carbon electrode is associated with a faradaic electrode.13,14

Carbon-based supercapacitors have been largely investigated because of their low cost, high cycle life, and high capacitance (measured in Farads [F]). Large-size (i.e., >5,000 F) devices are commercially available from companies such as Maxwell, Epcos, and Panasonic.15,16 This work focuses on the use of SWCNTs to enhance the performance of carbon-based supercapacitors.

Carbon Nanotubes

Carbon nanotubes, first reported and characterized by Iijima17 and Endo,18 consist of high-aspect-ratio cylinders of carbon that are often capped with hemispherical buckminster fullerences (i.e., C60” bucky balls). These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their understanding. Carbon nanotubes may be sub-classified as being SWCNTs, (sometimes abbreviated SWNT) or concentric multi-walled nanotubes (MWCNTs or MWNTs). Due to their impressive material properties, CNTs are being developed for use in applications such as superconductors,19 hydrogen storage,20 field emission, logic circuits,21 and numerous other emerging areas.

Supercapacitors

Both MWCNTs and SWCNTs have been researched for supercapacitor applications. In this work, SWCNTs are used. To understand the benefits of SWCNT-based supercapacitors, it is useful to begin with a first-principles approach to energy storage. The capacitance, C, of a material is given by Equation 1, where A is the geometric surface area of the electrode, εr is the permittivity of free space, ε is the relative permittivity of the dielectric material, and d is the distance between the two oppositely biased electrodes. (Note: All equations are given in the table on this page.)

Supercapacitors consist of two electrodes immersed in or impregnated with an electrolyte solution with a semi-permeable membrane serving as a separator23 that prevents electrical contact between the two electrodes but allows for ionic diffusion. When an electric potential is applied to the electrodes, a potential difference is created at the electrode-electrolyte interface. This electrostatic interface consists of a double layer between ions in the electrolyte and the electronic charges on the electrode24 (Figure 2). The interplane distance, d, in this system. As is evident from Equation 1, in order to achieve high capacitance, a material with high surface area (A) and small Helmholtz distance (d) should be chosen.25 Surface conditions are extremely important for capacitance, with porosity playing a large role.

The most prevalent materials being investigated for use in commercial-scale supercapacitors are activated carbons. This work will investigate SWCNT-based active electrode materials, but understanding the limitation of activated carbon electrodes is essential to realizing the full potential applicability and commercial feasibility of SWCNT-based supercapacitors.

Activated carbons are high-surface-area, high-porosity carbons made of small hexagonal rings organized into graphene sheets. These sheets can be produced by various processing methods that result in varying pore size distributions and orientations. Activated carbons lack long-range order and can therefore be viewed as a mixture of microdomains of ordered graphene sheets. The specific double-layer capacitance can be seen as the sum of each microdomain capacitance.

Qu25 has shown that these microdomains can be considered as a few graphene sheets stacked in parallel with thickness L. The sheets are linked together throughout the lateral direction and separated by a distance L. The specific capacitance of the activated carbon was shown to be proportional to the aspect ratio of the graphene sheets (i.e., L/L). A key to achieving large capacitance is increasing L while at the same time reducing L. Single-wall carbon nanotubes, with their extremely high aspect ratio, are therefore superb candidates for use in supercapacitor applications.

Pore sizes are classified according to the International Union of Pure and Applied Chemistry. Micropores are defined as having a radius less than 20Å.

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**Equations**

\[ C = \frac{\varepsilon_r \varepsilon}{d} \]  
\[ C = \frac{I}{\Delta V} \]  
\[ R_{ESR} = \frac{\Delta V}{I} \]  

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**Table I. Mean Capacitance, ESR, and Specific Capacitance**

<table>
<thead>
<tr>
<th>Type</th>
<th>Mean Capacitance (F)</th>
<th>Specific Capacitance (F/g)</th>
<th>ESR* (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiPco + Acetonitrile (unloaded)</td>
<td>0.2</td>
<td>0.1</td>
<td>7.8</td>
</tr>
<tr>
<td>Elicarb + Acetonitrile (unloaded)</td>
<td>0.6</td>
<td>0.4</td>
<td>8.4</td>
</tr>
<tr>
<td>Elicarb + Acetonitrile (loaded)</td>
<td>0.9</td>
<td>0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>PC10</td>
<td>10.0</td>
<td>1.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* ESR = equivalent series resistance
Mesopores have a radius between 20Å and 50Å, and macropores are any pores larger than 50Å. Activated carbon contains a wide distribution of pore sizes. Typical Brunauer, Emmett, and Teller (BET) surface areas for activated carbon are 1,000–3,000 m²/g. Unfortunately, a substantial fraction of this surface area resides in micropores or unpercolated pores which are inaccessible to ion migration and therefore unable to support an electrical double layer. Ions are capable of migration to some of the larger pores, although this results in an increased resistance in the electrolyte. Typically, such an increase in resistance results in decreased capacitance.

Carbon nanotubes offer an advantage over active carbon in terms of porosity. Although the BET surface area of CNT-based active materials is sometimes not as high as in activated carbon, Niu reports that the surface area is more accessible in CNTs. The pores are percolated and their size distribution lies mostly within the extremely beneficial mesopore range. In addition, the volume of deleterious micropores in samples of CNTs is negligible. Carbon nanotubes also offer chemical and mechanical stability. They have additional material and electrical properties that make them attractive candidates as an active material in a supercapacitor electrode. For example, the ballistic electrical conductivity of an arm-chair SWCNT is idyllic.

Single-wall carbon nanotubes were investigated in this study for increasing the power performances of carbon-based supercapacitors. This article presents performance characterizations of laboratory-scale supercapacitors assembled from treated aluminum current collectors coupled with a SWCNT-containing active electrode teamed with various electrolytes. Commercially available supercapacitors are also investigated and compared to the research results. Experimental procedures are presented in the sidebar.

**RESULTS & DISCUSSION**

**Laboratory-Scale SWCNT-Based Supercapacitors**

The constant voltage plot for the laboratory-scale supercapacitors reports the current pulse generated upon “firing” a supercapacitor that has been charged with a 1.5 V potential for approximately 5 s. For this evaluation, superior performance is based on a greater magnitude of the current pulse. The slight difference in the time application of the pulses on the horizontal axis is due to the manual firing of the supercapacitor by the operator every 4 s to 5 s and should not be interpreted as a performance metric.

The performance of SWCNT-based supercapacitors in comparison to the commercial benchmark reveals the importance of electrolyte selection (Figure 3). The difference in performance between the various room-temperature ionic liquids (RTIL) electrolytes is primarily attributed to the differences in ion size and viscosity between the electrolytes and therefore the diffusivity of the ions that are the charge carriers in the supercapacitor is impacted.

Room-temperature ionic liquids #1 and #4 behaved quite poorly. As shown in Figure 3, they were virtually indistinguishable from the horizontal axis. However, several electrolytes performed on par or superior to the commercial benchmark. Room-temperature ionic liquid #2 performed nearly identically to the commercial benchmark in pulse height. Note, however, that the commercially available product discharges more rapidly than RTIL #2. The superior performance of the SWCNT-based supercapacitors compared to the commercial benchmark becomes even more striking when comparing the response of the acetonitrile and tetraethylammonium tetrafluoroborate electrolyte (Figure 4).

In addition, it can be seen that the Elicarb SWCNT (if Figure 4 is extrapolated beyond the 1.05A equipment limitation) seems to offer superior performance compared to the HiPco SWCNTs. Yet, Figure 5 and Figure 6 show that when RTILs #2 and #5 are used, an opposite response occurs whereby the HiPco SWCNTs offer superior performance. These differences in performance are believed to be attributed to a mating effect, whereby a particular electrolyte ion diameter is better suited for the given porosity and material properties of either the HiPco or Elicarb SWCNTs.

Unfortunately, the laboratory-scale samples exhibited very poor reliability. This is attributed to the primitive nature of the kapton tape sealing method. The crudeness of this technique allowed for the electrolyte to suffer severe degradation within a few dozen hours of manufacture. The commercial benchmark samples from Maxwell have yet to degrade over the program period. This is, of course, to be expected with a commercially available product with a high level of quality control such as the PC10.

Yet, if the kapton seal on the laboratory-scale samples was opened and the active material re-saturated with the designated electrolyte, and then subsequently re-sealed, the supercapacitor performed in a manner similar to its original performance (Figure 8). This shows that if commercial-grade packaging and sealing technologies are employed, the SWCNT-based supercapacitors and electrolytes would have sufficient longevity that they could be used in mission-critical applications.

**Electrical Testing and Materials Characterization**

The constant current plot for the laboratory-scale supercapacitors reports a voltage change as the supercapacitor is charged at constant current.

The three experimental supercapacitors submitted to NASA for electrical screening were the HiPco SWCNT with acetonitrile electrolyte, the Elicarb SWCNT with acetonitrile, and the HiPco SWCNT with RTIL #2. Following an extended aging period of several weeks, it was expected that the electrolyte would have evaporated or deteriorated by the time testing occurred. A vial of acetonitrile was supplied for refilling the supercapacitors. No additional supply of the
RTILs was available at the time of the NASA-Johnson Space Center testing, so the supercapacitor with RTIL #2 was tested without refill. This supercapacitor behaved as a resistor, so its data is not included here. Room-temperature ionic liquid #5 had not been tested by the NASA-Johnson Space Center group at the time of this writing.

The performance of SWCNT-based supercapacitors in comparison to the commercial benchmark is seen in Figure 9. The Maxwell PC10 capacitor accepted charge for 60 s, but the HiPco + acetonitrile supercapacitor began to saturate after about 10 s. The charge time was reduced accordingly, and a plot of all data on this reduced timescale is shown in Figure 10.

An ideal charging curve resembles that of the Maxwell PC10 data—linear during charging and level once the current is shut off, though the constant voltage is offset by an instantaneous drop due to equivalent series resistance (ESR). It can be seen that most tests involving the experimental supercapacitors showed nonlinear charging, which are related to high ESR and leakage current, or in some cases due to the supercapacitor saturating with charge. Voltage also dropped off when current was turned off, rather than holding constant.

Capacitance, $C$, can be determined from constant-current charging as shown in Equation 2, where $I$ is the constant charging current, $t$ is the time charged, and $\Delta V_1$ is the increase in voltage during the linear portion of the charging period. Therefore, capacitance is related to the slope of the linear portion of the charging curve. The ESR can be determined by Equation 3, where $I$ is the constant charging current and $\Delta V_2$ is the magnitude of the instantaneous drop in voltage after the current is shut off. Mean capacitance, ESR, and specific capacitance data are presented in Table I for the acetonitrile-based supercapacitors.

**CONCLUSIONS**

This work has demonstrated that by altering the electrolyte composition and active electrode material attributes, carbon-nanotube-based supercapacitor performance can be significantly altered. Improved packaging and sealing techniques are expected to markedly reduce ESR and leakage current in the experi-
mental supercapacitors. The application of external pressure may decrease ESR. However, high pressure might also degrade the nanotube electrodes, hindering interaction between the electrode and electrolyte, or destroy the separator, causing electrical shorting.

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