

Carbon Nanotube-Based Supercapacitors: Technologies and Markets

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ABSTRACT:

Electrochemical double-layer capacitors (also known as “supercapacitors” or “ultracapacitors”) have tremendous potential as high-energy and high-power sources for use in low weight hybrid systems. Commercial applications for such devices include uninterruptible power applications, telecommunications, and public transportation. Electrodes based on carbon nanotubes (CNTs) offer exceptional power and energy performance due to the high surface area, high conductivity, and the ability to functionalize the CNTs to optimize capacitor properties. In this article, a team of researchers at Georgia Tech Research Institute report on the preparation of electrochemical capacitors incorporating CNT electrodes and their performance compared with existing commercial technology. Preliminary results indicate that substantial increases in both power and energy density are possible with further development. The authors discuss the effects of nanotube growth and processing methods, including purification and functionalization, on electrochemical capacitor performance. Finally, the authors review the compatibility of different CNTs and electrolytes by summarizing research focused on varying the type of electrolyte ions that accumulate on the high surface area electrodes.

I. INTRODUCTION

The late Nobel Laureate Richard Smalley was a strong proponent of the benefits of nanotechnology to overcome global energy dilemmas. Energy storage devices are classified according to energy and power density. Power density is related to the “strength” (wattage) of a given current and voltage combination, while energy density is related to the duration of time that wattage can be applied. Electrochemical double layer (ECDL) capacitors (also abbreviated EDLC), commonly called “supercapacitors” or “ultracapacitors” are intermediate systems that bridge the power/energy gap between traditional dielectric capacitors (high power) and batteries (high energy).¹

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¹ Thomas A. Reynolds, *Development of Carbon-Nanotube/Polymer Composites*, TECH BRIEFS, June 2005, at 70.

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.² 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 to 455 Wh/kg.³ Rechargeable Ni-Cd batteries can achieve 1,000 cycles in a lifetime, with an energy density of approximately 225 Wh/kg.⁴

Conventional capacitors traditionally have much higher power densities than batteries, ranging from 1.0×10^2 to 2.7×10^{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 which require a large amount of energy storage or delivery.

ECDL supercapacitors have properties ranging between these two common energy storage devices. Supercapacitors offer high power density, high energy density and long cycle life.⁵ 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.⁶

A recent study by a team of entrepreneurs at U.C. Davis found many potential applications ranging from industrial power applications such as forklifts and other machine specific needs to public transportation.⁷ They claim that ECDL capacitors can be integrated into light rail applications to provide surge power for acceleration and can then be regeneratively charged during braking. Currently in France, light rail trains have already incorporated standard (non-CNT-based) ultracapacitors into functional light rail systems. The telecommunications industry has lately expressed significant interest in ECDL capacitors to provide bridge power for uninterrupted operation of server farms and switching stations. Aerospace and military applications are already the first adopters of CNT-based supercapacitors. The Ready group at Georgia Tech has worked with NASA and the Space and Missile Defense Command (SMDC) to develop CNT-based supercapacitors since 2003. The evolution of the lab-scale research to a marketable product has shown promise by using alternate electrolytes in the ECDL structure. Supercapacitors incorporating CNTs can potentially store higher energy density than traditional capacitors with an equivalent amount of delivered power (see Figure 1).

Three main classes of supercapacitors are described in the literature: metal oxide,⁸ electronically conducting polymer,⁹ and carbon-based supercapacitors.¹⁰ Recently, hybrid supercapacitors have been developed where an activated carbon electrode is associated with a faradaic electrode.¹¹

² Thomas Christen & Martin W. Carlen, *Theory of Ragone Plots*, 91 J. POWER SOURCES 210-16 (2000).

³ *Principle Dry Battery Systems*, http://data.energizer.com/PDFs/typical_characteristics.pdf (last visited Jan. 22, 2007).

⁴ C. Emmenegger, et al., *Investigation of Electrochemical Double-layer (ECDL) Capacitors Electrodes Based on Carbon Nanotubes and Activated Carbon Materials*, 124 J. POWER SOURCES 321-29 (2003).

⁵ M. Endo, et al., *High Power Electric Double Layer Capacitors (EDLC's) Form Operating Principle to Pore Size Control in Advanced Carbons*, 1 CARBON SCI. 117-28 (2001).

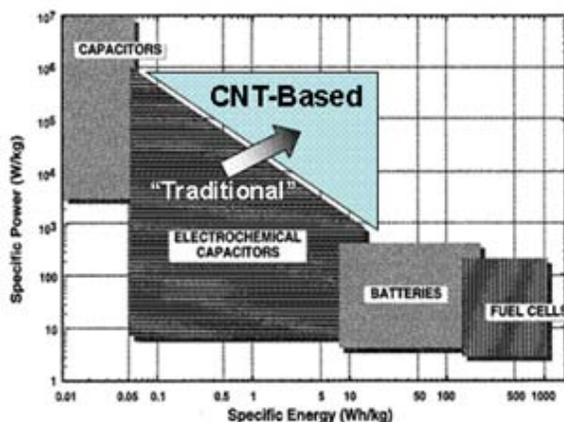
⁶ B. E. CONWAY, *ELECTROCHEMICAL SUPERCAPACITORS—SCIENTIFIC FUNDAMENTALS AND TECHNOLOGICAL APPLICATIONS* (1999).

⁷ J. GAYMAN, ET AL., *ADVANCED ENERGY STORAGE DEVICES* (prepared for the U.C. Davis Graduate School of Management).

⁸ Q. L. Fang, et al., *Ruthenium Oxide Film Electrodes Prepared at Low Temperatures for Electrochemical Capacitors*, 148 J. ELECTROCHEM. SOC. A833-A837 (2001); J. Jiang & A. Kucernak, *Electrochemical*

Carbon-based supercapacitors have been largely investigated because of their low-cost, high cycle-life and high capacitance. Large-size (i.e., >5000 F) devices are commercially available from companies such as Maxwell, Epcos, and Panasonic.¹² In this article, we focus on the use of CNTs to enhance the performance of traditional carbon-based supercapacitors.

FIGURE 1: GENERIC PLOT OF SPECIFIC POWER VERSUS SPECIFIC ENERGY FOR VARIOUS POWER/ENERGY SOURCES.



Supercapacitor Material Based on Manganese Oxide: Preparation and Characterization, 47 ELECTROCHIM. ACTA 2381-88 (2002).

⁹ M. Mastragostino, et al, *Conducting Polymers as Electrode Materials in Supercapacitors*, 148 SOLID STATE IONICS 493-98 (2002); W.-C. Chen, et al., *Polyaniline-deposited Porous Carbon Electrode for Supercapacitor*, 48 ELECTROCHIM. ACTA 641-49 (2003).

¹⁰ D. Lozano-Castello, et al., *Influence of Pore Structure and Surface Chemistry on Electric Double Layer Capacitance in Non-aqueous Electrolyte*, 41 CARBON 1765-75 (2003); J. Gamby, et al., *Studies and Characterisations of Various Activated Carbons Used for Carbon/Carbon Supercapacitors*, 101 J. POWER SOURCES 109-16 (2001).

¹¹ A. Laforgue, et al., *Activating Carbon/Conducting Polymer Hybrid Supercapacitors*, 150 J. ELECTROCHEM. SOC. A645-A651 (2003); A. DuPasquier, et al., *A Comparative Study of Li-Ion Battery, Supercapacitor and Nonaqueous Asymmetric Hybrid Devices for Automotive Applications*, 115 J. POWER SOURCES 171-78 (2003).

¹² A. Chu & P. Braatz, *Comparison of Commercial Supercapacitors and High-power Lithium-ion Batteries for Power-assist Applications in Hybrid Electric Vehicles: I. Initial Characterization*, 112 J. POWER SOURCES 236-46 (2002); R. Kötz & M. Carlen, *Principles and Applications of Electrochemical Capacitors*, 45 ELECTROCHIM. ACTA 2483-98 (2000).

II. CARBON NANOTUBES: AN OVERVIEW

CNTs were first reported and characterized by Iijima¹³ and Endo.¹⁴ CNTs consist of high-aspect ratio cylinders of carbon that are often “capped” with hemispherical buckminster fullerenes (i.e., C₆₀, or “bucky balls”). These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their understanding.

CNTs may be sub-classified as being single walled (SWCNTs—sometimes abbreviated SWNT) or concentric multi-walled nanotubes (MWCNTs or MWNTs).

III. SUPERCAPACITORS: AN OVERVIEW

Both MWCNTs and SWCNTs have been researched for supercapacitor applications. To understand the benefits of CNT-based supercapacitors, it is useful to begin with a first-principles approach to energy storage. The capacitance, *C* (measured in Farads, F), of a material is given by:

$$C = \frac{\epsilon_o \cdot \epsilon_r \cdot A_E}{d}$$

where *A_E* is the geometric surface area of the electrode, ϵ_o is the permittivity of free space, ϵ_r is the relative permittivity of the dielectric material and *d* is the distance between the two oppositely biased electrodes.

Supercapacitors consist of two electrodes immersed in or impregnated with an electrolyte solution with a semi-permeable membrane serving as a separator⁴¹⁵ that prevents electrical contact between the two electrodes, but which 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 electrode (see Figure 2).¹⁶

The interplane distance, *d*, in the above equation is now reduced to the Helmolz double layer distance, *d_D*, defined as half the diameter of the adsorbed solvated ions at the electrode/electrolyte interface. In supercapacitors, energy storage is due to the separation of electronic and ionic charges at the interface between a high surface-area active electrode and the electrolyte solution.

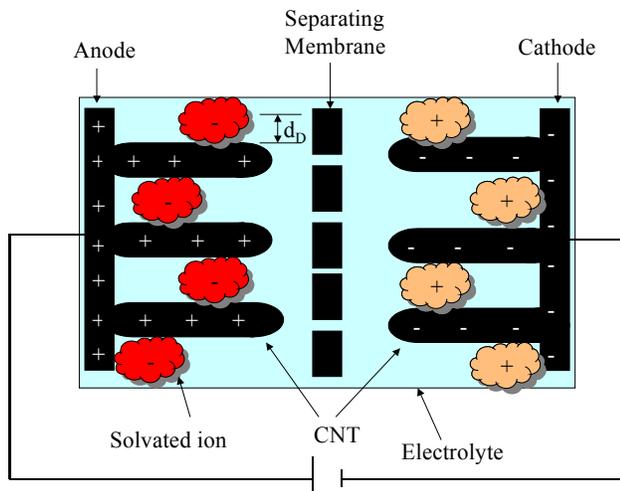
¹³ S. Iijima, *Helical Microtubuals of Graphitic Carbon*, 354 NATURE 56 (1991).

¹⁴ A. Oberlin, et al., *Filamentous Growth of Carbon through Benzene Decomposition*, 32 J. CRYST. GROWTH 335-49 (1976).

¹⁵ See Emmenegger, et al., *supra* note 4.

¹⁶ See S. Arepalli, et al., *Carbon-Nanotube-Based Electrochemical Double-Layer Capacitor Technologies for Spaceflight Applications*, Dec. JOM 26 (2005), http://eosl.gtri.gatech.edu/micro/JReady_Dec_2005_JOM_FINAL.pdf.

FIGURE 2: GENERIC SCHEMATIC OF ELECTROCHEMICAL DOUBLE LAYER CAPACITOR (NOT TO SCALE)



IV. A COMPARISON OF ACTIVATED CARBON AND CARBON NANOTUBES AS THE ELECTRODE MATERIAL

The active material on the electrode is an essential part of the supercapacitor system. As is evident from the equation above, in order to achieve high capacitance, a material with high surface area (A_E) and small Helmholtz distance (D_d) should be chosen.¹⁷ 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. Activated carbons are extremely cheap and come from various readily-available sources (such as charred coconut husks). As such, the justifications involved in their replacement with CNTs must be compelling and are often not purely economic based, but rather are performance driven. Understanding the limitation of activated carbon electrodes is essential to realizing the full potential applicability and commercial feasibility of CNT-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.

Qu has shown that these microdomains can be considered as a few graphene sheets stacked in parallel with thickness L_c .¹⁸ The sheets are linked together throughout the lateral direction and separated by a distance L_a . The specific capacitance of the activated carbon was shown to be proportional to the aspect ratio of the graphene sheets (i.e., L_c/L_a). A key to achieving large capacitance is increasing L_c , while at the same time reducing L_a .

¹⁷ D. Qu, *Studies of the Activated Carbons used in Double-layer Supercapacitors*, 109 J. POWER SOURCES 403-11 (2002).

¹⁸ *Id.*

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 unpercolated pores which are inaccessible to ion migration and therefore unable to support an electrical double layer.¹⁹ Ions are capable of migration to some of the larger pores, though this results in an increased resistance in the electrolyte, which typically results in decreased capacitance.

There are several reasons why CNT-based electrodes may ultimately outperform activated carbon in supercapacitors.²⁰ Nanotubes have high conductivity, large surface area (1 to >2000 m²/g), good corrosion resistance, high temperature stability, percolated pore structure, and can be functionalized to optimize their properties. MWNT supercapacitors have been found to have specific capacitances of 4 to 135 F/g as determined by cyclic voltammetry, impedance spectroscopy, and dc discharge using 6 mol/l KOH as an electrolyte.²¹

Perhaps the primary benefit of percolated CNT electrodes over activated carbon electrodes is the opened mesopores formed by the accessible interconnected network of nanotubes. 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.²² The pores are percolated and their size distribution lies mostly within the extremely beneficial mesopore range. The volume of deleterious micropores in samples of CNTs is also negligible. CNTs also offer chemical and mechanical stability.

CNTs are also more conductive than activated carbon. CNTs are comprised of a mix of metallic, semiconducting, and insulating materials. Each tube will exhibit different electrical behavior depending on its chirality. Chirality is best explained as the geometry of which a periodic condition can be enforced about the circumferential direction of the tube structure. There is no congruent chirality type for a mass of tubes and this means there is a mix of different conductive and semiconductive CNT materials in any batch.

It has been found that acid treated nanotube electrodes have improved electron transfer kinetics.²³ Acid treatment facilitates electron transfer and creates the existence of more surface area, also referred to as the availability of adsorption sites. This acid treatment acts to functionalize the CNT. Overall, the electron transfer kinetics of CNTs exceed those of other carbons. This is partly due to the band structure of metallic CNTs, which have increased electron transfer rates. Some of this conductivity difference can be related to the highly delocalized pi bonds on the outer surface of the CNT.

Notwithstanding the benefits of nanotubes, at the time of this writing, nanotube-based supercapacitors do not outperform the best supercapacitors fabricated with activated carbon. However, ongoing research activities in deposition and treatment of the nanotubes promise to increase the performance of the electrodes.

¹⁹ C. Niu, et al., *Electrochemical Synthesis of Polypyrrole/Carbon Nanotube Nanoscale Composites Using Well-aligned Carbon Nanotube Arrays*, 70 APPL. PHYS. LETT. 1480 (1997).

²⁰ E. Frackowiak, et al., *Nanotubular Materials as Electrodes for Supercapacitors*, 77-78 FUEL PROCESS. TECHNOL. 213-219 (2002); Ch. Emmenegger, et al., *Carbon Nanotube Synthesized on Metallic Substrates*, 162-163 APPL. SURF. SCI. 452-56 (2000); see also A.K. Chatterjee, et al., *CVD Synthesis of Carbon Nanotubes Using a Finely Dispersed Cobalt Catalyst and Their Use in Double Layer Electrochemical Capacitors*, 48 ELECTROCHIM. ACTA 3439-46 (2003).

²¹ E. Frackowiak, *Supercapacitor Electrodes from Multiwalled Carbon Nanotubes*. 77 APP. PHYS. LETT. 2421-23 (2000); E. Frackowiak & F. Beguin. *Electrochemical Storage of Energy in Carbon Nanotubes and Nanostructured Carbons*, 40 CARBON 1775-87 (2002).

²² Niu, *supra* note 19.

²³ P. Papakonstinou, et al., *Fundamental Electrochemical Properties of Carbon Nanotube Electrodes*, 13 FULLER. NANOTUB. CARBON NANOSTRUCTURES 275-85 (2005).

Several groups are developing different deposition strategies to enhance CNT electrode performance. For example, a recent study used a binder free MWNT electrode film fabrication method called electrostatic spray deposition.²⁴ The technique showed a well-entangled and interconnected porous structure on the nanometer scale, and with the experimental setup achieved specific capacitance of 108 F/g at a scan rate of 10mV/s and a slight decrease at a 100mV/s scan rate to 103 F/g.²⁵ The difference in specific capacitances can be attributed to the altered diffusivity of the ionic species under the varying voltage scan rates. It is interesting to note that this electrode type did not require a binder for the CNT and showed good performance. The typically insulative binder acts to increase the effective resistance of the CNT electrode and decrease performance.

Techniques to increase the adsorption sites available to ions in CNT structures are also being pursued. A sample of SWNT has varying types of adsorption sites.²⁶ The accessibility to these sites by small molecules changes with the bundle morphology and purification process. Thus, one avenue to open new adsorption sites is increasing the purity of the nanotubes. It was found that purified CNTs performed orders of magnitude better than as-is CNT electrodes (non-purified CNTs) in the same experimental setup.²⁷ Experiments implemented a binder solution (carboxymethylcellulose and distilled water) to make a paste electrode material that could effectively be spread on a current collector (in these cases a piece of metal foil).²⁸ In the paste electrode method, the specific capacitance ranged widely depending on the CNT manufacturing method—from 10 F/g for chemical vapor deposition MWNT to 79 F/g for fluidized-bed MWNT.²⁹ When prepared as a fully functioning package (rather than solely lab-based electrodes), a specific capacitance of 0.6 F/g was found for a MWNT ECDL cell.³⁰

Functionalization and coating strategies are also being developed to optimize performance. For example, one group has shown that composite films of MWNT and ruthenium oxide (RuO₂) had an energy storage density that increased about three times as compared to MWNT treated with piranha solution (a hydrofluoric acid solution).³¹ The RuO₂ coated nanotubes had improved electron and ion transfer. The creation of metal centers within the CNT material should increase the energy density of the ECDL supercapacitor by providing multiple redox reactions. RuO₂ notably shows great performance due to its multiple oxidation states. The excellent performance of the MWNT composites is related to the high surface area, conductivity, and electrolyte accessibility of the nanoporous structure.

Performance can also be increased via oxygenated functionalization and polypyrrole (PPy) coatings of nanotubes. Again, the open entangled network of the PPy-coated nanotubes favors the formation of a percolated three dimensional Helmholtz double layer in the bulk. Performance increases of CNT over the best activated carbons have the basic relation of an increase in percolated surface area, but the increase in capacitor performance is not as simple as an increase in surface area of the electrode. To some extent the ions of the electrolyte must be adsorbed into the electrode material penetrating a layer of about 100nm into the surface.

²⁴ J. Kim et al., *Fabrication and Electrochemical Properties of Carbon Nanotube Film Electrodes*, 44 CARBON 1963-68 (2006).

²⁵ *Id.*

²⁶ S. Agnihotri, et al., *Adsorption Site Analysis of Impurity Embedded Single-walled Carbon Nanotubes*. 44 CARBON 2376-83 (2006).

²⁷ Arepalli, et al., *supra* note 16.

²⁸ See Emmenegger, et al., *supra* note 4.

²⁹ *Id.*

³⁰ See Arepalli, et al., *supra* note 16.

³¹ J. Lee & H. Pathan, *Electrochemical Capacitance of Nanocomposite Films Formed by Loading Carbon Nanotubes With Ruthenium Oxide*, 159 J. POWER SOURCES 1527-31 (2006).

V. OPTIMIZING THE ELECTROLYTE FOR NANOTUBE-BASED SUPERCAPACITORS

Developing CNT-based supercapacitors that are commercially superior to supercapacitors comprising activated carbon also requires identifying and optimizing the appropriate electrolyte. An electrolyte is a solution which contains ions that behave as an electrically conductive medium. Electrolytes in chemistry commonly exist as solutions of acids, bases, or salts. The electrolyte that is used in the supercapacitor can play a significant role in the power and energy densities achieved. If the electrolyte breaks down at relatively low voltages, the ECDL cell may not have a sufficiently high energy or power density.

It is the diffusion and movement of these ions that allows the build up of opposing charges at the electrode interface that leads to charge storage. When no potential bias is applied to the capacitor the ions in the electrolyte are randomly distributed. Once there is a potential bias, anions are attracted to the positive electrode layer and cations conversely go to the negative electrode layer. Thus, factors that impede the motion of the ions can lead to a poorly performing supercapacitor. With any mechanism that involves diffusion through matter (in this case the ions through the separating membrane, or into the adsorption sites of the CNT electrodes), several parameters can affect ionic motion: electrolyte ion size, electrolyte viscosity, surface wettability, and electrolyte molecular weight.

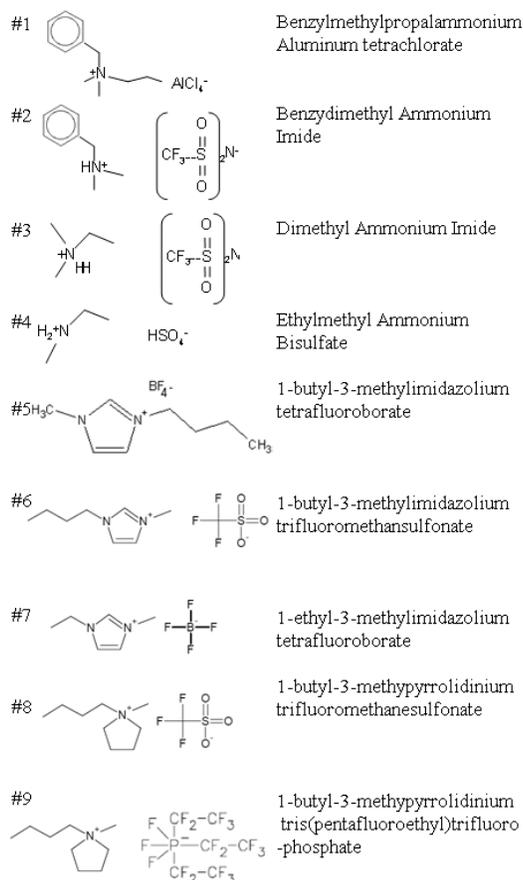
The ideal EDLC has the highest surface area possible with as many ions as possible reaching the surface without being impeded. The chemical nature (bond structure, mass, reactivity, acidity, etc.) of the electrolyte is of concern for how it affects the movement of the ions through the separating membrane and to the electrode surface. To some extent there is a diffuse-layer ion distribution at the electrodes.³²

A type of electrolyte called a room temperature ionic liquid (RTIL) can be used in supercapacitors. These liquids are electrolyte solutions with a melting temperature below that of room temperature. The Ready group at Georgia Tech has looked at a variety of RTILs and found significant performance differences (see Figure 3).³³

³² See CONWAY, *supra* note 6.

³³ Arepalli, et al., *supra* note 16.

FIGURE 3: WORK OF THE READY GROUP.



Work by the Ready group has demonstrated that by altering the electrolyte composition and active electrode material attributes, CNT-based supercapacitor performance can be markedly altered. The results from constant current and constant voltage tests included specific capacitance and equivalent series resistance (ESR) determinations. Improved packaging and sealing techniques are expected to markedly reduce ESR and leakage current in the experimental supercapacitors as they advance towards a marketable product.