Carbon Nanotube-Based Supercapacitors

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ABSTRACT

Due to the need for increased power performance, supercapacitors are emerging as an alternative to conventional electric energy storage devices. Because of their unique properties, carbon nanotubes are a promising material for next generation supercapacitors. Specifically, the use of nanotubes to construct supercapacitor electrodes can increases the power density and performance of supercapacitors relative to conventional dielectric capacitors. The authors explain different methods of constructing supercapacitors using nanostructure materials and also outline the benefits of this innovative form of energy storage.

I. SUPERCAPACITORS

Of all the challenges facing human beings in the near future, energy related issues are likely to be the grandest. To achieve a more sustainable society with adequate renewable energy and less environmental pollution, more versatile, robust and efficient approaches in electric energy storage and conversion are needed.

Electric energy storage devices may be broadly characterized by two parameters—energy density (how long the device can last) and power density (how much of that energy can be delivered from the device over a certain period of time). Batteries have been the preferred electricity storage device because of their portability and relative high energy density for many applications requiring sustained power supply over a reasonable time period. However, for other applications demanding a huge power surge or instantaneous power release like rocket launching, batteries become unsuitable due to their slow rate of energy release. Although new technologies such as the lithium-ion battery have been developed to improve the power performance (high-rate capability), they are still subject to the same intrinsic limits. Supercapacitors, also called ultracapacitors or electrochemical capacitors, are thus emerging as the promising energy sources with exceptionally fast charge-discharge rates.

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Unlike dielectric capacitors that store energy in the form of separated electrical charge, supercapacitors store energy electrostatically by polarizing an electrolytic solution.[1] They are similar in design and manufacture to batteries in that both have two electrodes immersed in an electrolyte with a separator between the two electrodes.[2] When a voltage is applied across the positive and negative electrodes of a supercapacitor, the ions in the electrolyte are attracted to the oppositely charged electrodes. Opposite charges are separated across the interface between the solid electrode surface and the liquid electrolyte in the micropores of the electrodes, creating a very thin "electrochemical double layer." Energy is thus stored in the form of charge separation between the double layer.[3]

In ordinary planar sheet dielectric capacitors, the capacitance inversely depends on the interelectrode separation. In contrast, the capacitance for a supercapacitor depends on the separation between the charge on the electrode and the countercharge in the electrolyte,[4] which is far smaller than that in the dielectric capacitor. As a result, supercapacitors have a very large capacitance. In general the capacitance of supercapacitors is about 100 times higher than that of comparable regular dielectric capacitors, and the peak power density is up to 100 times higher than that of batteries.

Supercapacitors have several advantages including high power density, excellent reversibility, very long cycle life, and quick mode of operation.[5] Among these, high power density is a particular strength, making them indispensable for surge-power delivery. The potential applications of supercapacitors include load-leveling functions for batteries in electrical vehicle and hybrid electrical vehicles during starting, acerbating, and regenerative braking, and burst-power generation in electronic devices such as personal computers, cell phones, camcorders, digital cameras, navigational devices, PDAs (personal data assistants), PCMCIA (Personal Computer Memory Card International Association) cards and flash cards, and medical devices.

Supercapacitors are categorized into electrochemical double layer capacitors (EDLC), the ones introduced above and pseudocapacitors.[6] As mentioned before, the energy storage mechanism for EDLC capacitance involves the separation of electronic charges at the interface between electrode and electrolyte, resulting in a Helmholtz layer;[7] whereas the pseudocapacitor is based on fast, reversible faradic redox reactions which occur between the oxide and the electrolyte, giving rise to the so-called pseudocapacitance. Because of the electrochemical redox reaction of the electrode materials, some faradic charge transfer takes place as in a battery, thus the capacitance in a pseudocapacitor is potentially much higher than that in an EDLC. On the other hand, since redox reactions are involved, the power performance is compromised.

Furthermore, since the capacitance of EDLC is proportional to the surface area, electrochemical inert materials with the highest specific surface area are the most favorable electrode materials so as to form a

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[1] B.E. CONWAY, ELECTROCHEMICAL SUPERCAPACITOR: SCIENCTIFIC FUNDAMENTALS AND TECHNOLOGICAL APPLICATION (1999).

[2] A.S. Arico, et al, *Nanostructured Materials For Advanced Energy Conversion and Storage Devices,* 4 NATURE MATERIALS 366-377 (2005).

[3] R. H. Baughman, et al, *Carbon Nanotubes - The Route Toward Applications.* 297 SCIENCE 787-792 (2002).

[4] *Id.*

[5] A. Burke, *Ultracapacitors: Why, How, and Where Is The Technology*, 91 J. POWER SOURCES 37-50 (2000).

[6] B.E. Conway and W.G. Pell, *Double-layer and Pseudocapacitance Types Of Electrochemical Capacitors and Their Applications To The Development of Hybrid Devices,* 7 JOURNAL OF SOLID STATE ELECTROCHEMISTRY 637-644 (2003).

[7] Burke, *supra* note 5. *See also* C. Emmenegger, et al, *Investigation of Electrochemical Double-layer (ECDL) Capacitors Electrodes Based On Carbon Nanotubes And Activated Carbon Materials,* 124 J. POWER SOURCES 321-329 (2003).

double layer with a maximum number of electrolyte ions.[8] Different carbonaceous materials including activated carbon, carbon fibers and carbon aerogels have been widely studied owing mainly to their high specific surface areas.

II. CARBON NANOTUBES

The performance of energy storage devices depends decisively on the properties of the materials they are made of; the innovation of materials thus lies at the heart of the advances in energy storage.[9] Supercapacitor technology can benefit significantly by moving from conventional to nanostructured electrodes, owing to the exceedingly huge specific surface area and other superior properties of the nanomaterials. In this sense, carbon nanotubes are the most promising electrode materials for supercapacitors.

Carbon nanotubes, long and thin cylinders of carbon, are a unique quasi one-dimensional nanomaterial. They were first reported by Iijima in 1991 when he discovered multi-walled carbon nanotubes (MWNTs) in carbon-soot made by an arc-discharge method.[10] Later, he also reported the single-walled carbon nanotubes (SWNTs).[11] Since then, carbon nanotubes have attracted intense research attention worldwide.

Carbon nanotubes can be thought of as graphene sheets with a hexagonal lattice that have been wrapped up into a seamless cylinder.[12] ("Graphene" refers to a single sheet of linked carbon atoms having the structure found in graphite). A SWNT is has a typical diameter in the order of 1-2 nm.[13] Whereas a MWNT consists of concerntric cylinders, much like the Russian matroyska dolls, with an interlayer spacing of 0.34 nm and a diameter typically in the order of several tens of nanometers.

Due to their unique structure, carbon nanotubes possess many remarkable properties, such as high specific surface area, high aspect ratio, remarkable electrical and thermal conductivity, chemical stability and low mass. In terms of mechanical properties, carbon nanotubes are among the strongest and most resilient materials known in nature.[14] The tensile strength of carbon nanotubes is about a hundred times higher than steel. They can tolerate large strains before mechanical failure, and their Young's modulus is about 1.2TPa (1TPa for SWNTs and 1.28TPa for MWNTs). The electrical properties of carbon nanotubes depend on the tube types. While MWNTs are generally all metallic, SWNTs can be either metallic or semiconducting, depending on the structure parameters such as the chirality. For metallic single-walled carbon nanotubes, the electric conductivity is on the order of 10^4 S/cm. The structural uniqueness and the intriguing properties of carbon nanotubes have led to intense research efforts in exploring their potential applications.[15] So far, researchers and companies have explored using carbon nanotubes (individually or as an assembly) as field emission sources, tips for scanning probe microscopy, nanotweezers, chemical sensors, electromechanical actuators, and composite reinforcement with improved mechanical, thermal or electrical properties. Their applications in electrochemical energy storage and conversion have also been proposed in recent years. For example, carbon nanotubes have

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[8] L. Diederich, et al, *Supercapacitors Based On Nanostructured Carbon Electrodes Grown By Cluster-Beam Eeposition*, 75 APPLIED PHYSICS LETTERS 2662-2664 (1999).

[9] Arico, et al., *supra* note 2.

[10] S. Iijima, *Helical Microtubules of Graphitic Carbon*, 354 NATURE 56 (1991).

[11] S, Iijima and T. Ichihashi, *Single-shell Carbon Nanotubes of 1-nm Diameter*, 363 NATURE 603 (1993).

[12] J.W.G. Wildoer, et al, *Electronic Structure Of Atomically Resolved Carbon Nanotubes*, 391 NATURE, 59 (1998).

[13] H.J. Dai, *Carbon Nanotubes: Opportunities and Challenges*, 500 SURFACE SCIENCE 218-241 (2002).

[14] B.I. Yakobson and R.E. Smalley, *Fullerene Nanotubes: C-1000000 and Beyond*, 85 AMERICAN SCIENTIST 324 (1997).

[15] H.J. Dai, *Carbon Nanotubes: Opportunities and Challenges*, 500 SURFACE SCIENCE 218 (2002).

been formed into electrodes for supercapacitors, for Li-ion secondary batteries, and for hydrogen storage in fuel cells.

III. APPLICATION OF CARBON NANOTUBES IN SUPERCAPACITORS

For supercapacitors, attaining a high power density is always the main goal.[16] The maximum power density of a supercapacitor is given by $P_{max}=V_i^2/4R$ (where V_i is the initial voltage and R is the equivalent series resistance (ESR)).[17] Thus, high power density requires low electrical resistance of the electrode itself and the contact resistance between the electrodes and current collectors. Clearly, there is a role for carbon nanotubes to play due to their remarkable specific surface area and electric conductivity.

In addition, the unique structure of carbon nanotubes is another advantage over conventional carbon materials. As carbon nanotubes usually have an aspect ratio of more than 1000, they tend to entangle with each other to form a durable and porous nanotube skeleton. Such a porous structure formed by the open spaces between entangled nanotubes enables easy access of the electrolyte ions to the electrode/electrolyte interface, which is crucial for charging the electric double layer, thus exhibiting extremely small resistance of the electrode itself. Moreover, due to the durability of the nanotube skeleton, little or even no binder is needed, unlike conventional carbon materials.

The pioneering work of using carbon nanotubes for double layer supercapacitors was carried out by Niu, *et al.*, who developed supercapacitor electrodes with free-standing mats of MWNTs.[18] Unlike other types of carbon electrodes containing micropores including slit and dead end pores, the pores in the carbon nanotube electrode are spaces in the entangled nanotube network, and are thus all inter-connected. Such nanotube electrodes are essentially open structures, enabling almost all the surface area accessible to the electrolyte. In contrast, in an activated carbon electrode with a surface area of 1000 m^2/g, only less than 1/3 of the surface area is available for the formation of an ionic double layer.[19] Consequently, a power density above 8 kW/kg was obtained using these nanotube electrodes.

The encouraging electrochemical performance of carbon nanotube electrodes has led to extensive studies in this area. A systematic work was done by Frackowiak, et al., to investigate the electrochemical characteristics and to correlate them with the microtexture and elemental composition of supercapacitors built from different type of MWNTs and SWNTs.[20] It was found that, in addition to the presence of mesopores formed by the entanglement of carbon nanotubes, the central canals of the tubes also contribute to easy accessibility of the ions charging the electrical double layer.

In general, SWNTs have been shown to have higher specific capacitance, due mainly to their large surface area. Frackowiak, et al., found, however, that MWNTs could generate capacitance twice as high in comparison to SWNTs under certain circumstance.[21] They suggested that the higher capacitance of MWNTs in their study was attributed to the presence of mesopores due to the open central canal and the accessible network of entangled nanotubes, facilitating the transport of the ions from the solution to the charged interface.

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16 Arico, *supra* note 2.
17 Conway, *supra* note 1.
18 C.M. Niu, et al, *High Power Electrochemical Capacitors Based on Carbon Nanotube Electrodes*, 70 APPLIED PHYSICS LETTERS 1480 (1997).
19 *Id.*
20 E. Frackowiak, et al, *Supercapacitor Electrodes From Multiwalled Carbon Nanotubes*, 77 APPLIED PHYSICS LETTERS 2421 (2000); E. Frackowiak and F. Beguin, *Carbon Materials For The Electrochemical Storage Of Energy In Capacitors*, 39 CARBON 937 (2001); E. Frackowiak, et al, *Nanotubular Materials For Supercapacitors*, 97 J. POWER SOURCES 822 (2001).
21 E. Frackowiak,, Nanotubular Materials For Supercapacitors, *supra* note 20.

Capacitance performance of carbon nanotubes is also dependent upon the surface condition of the nanotubes. Carbon nanotubes chemically modified by strong acid oxidation have demonstrated a well defined pseudocapacitance behavior due to the Faradaic redox reactions of their rich surface functionality.[22] However, it is noteworthy that the capacitance gradually decreased during a long cycling. Hence, even if the value of the specific capacitance increased significantly because of the increased overall pseudocapacitance (an increase from 80 to 137F/g in one study[23] and 22 to 56 F/g in another study[24]), the fading part of the capacitance has very limited practical meaning. Therefore, this kind of supercapacitor in essence is still an EDLC.

Similar pseudocapacitance behavior evidenced by the broad redox responses has also been observed in electrodes built from SWNTs, though it is not clear whether it was due to the presence of oxygen-containing functional groups attached to the surface of the nanotubes or to the impurities retained after purification in nitric acid. These redox responses can be eliminated by annealing the material at high temperature.

IV. HIGH POWER DENSITY SUPERCAPACITORS USING CARBON NANOTUBE THIN FILM ELECTRODES

A supercapacitor is useful because of its high power density (at least about ten times larger than that of batteries). Several successful attempts to fabricate high power density supercapacitors have been reported.

One group obtained a power density of 20 kW/kg in an electrolyte of 7.5 N KOH.[25] A polished nickel foil was used for lower contact resistance and a heat-treatment at high temperature was used to reduce the internal resistance of the SWNT electrode. Direct growth of carbon nanotubes on metal current collectors is another way to reduce the contact resistance as realized by Yoon, et al., using hot filament plasma enhanced chemical vapor deposition (HFPECVD).[26] A much higher discharge efficiency and good electrodynamic performance were obtained, resulting in higher power density.

The Pan group at University of California, Davis has developed two different approaches to lower the equivalent series resistance in fabricating carbon nanotube thin film electrodes.[27] One approach is to prepare thin films with coherent structures using highly concentrated colloidal suspension of carbon nanotubes, resulting in very high packing density and some local alignment (Figure 1(a)) of the nanotubes. This coherent and flexible film was a highly conductive nanotube network with drastically small electrode resistance. In addition, the nanotubes adhered directly to the current collector since no binder was added, thus the contact between them was very good and contact resistance was reduced as

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[22] E. Frackowiak, et al, *Supercapacitor Electrodes From Multiwalled Carbon Nanotubes*, *supra* note 20; E. Frackowiak and F. Beguin, *Carbon Materials For The Electrochemical Storage of Energy In Capacitors*, *supra* note 20.

[23] E. Frackowiak, et al, *Supercapacitor Electrodes From Multiwalled Carbon Nanotubes*, *supra* note 20.

[24] C.S. Li, et al, *A Study Of Activated Carbon Nanotubes As Double-layer Capacitors Electrode Materials*, 58 MATERIALS LETTERS 3774 (2004).

[25] K.H. An, et al, *Supercapacitors Using Single-Walled Carbon Nanotube Electrodes*, 13 ADVANCED MATERIALS 497 (2001); K.H. An, et al, *Electrochemical Properties Of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes*, 11 ADVANCED FUNCTIONAL MATERIALS 387 (2001).

[26] B.J. Yoon, et al, *Electrical Properties of Electrical Double Layer Capacitors With Integrated Carbon Nanotube Electrodes*, 388 CHEM. PHYS. LETT. 170 (2004).

[27] C.S. Du, et al, *High Power Density Supercapacitors Using Locally Aligned Carbon Nanotube Electrodes*, 16 NANOTECHNOLOGY 350 (2005); C.S. Du, et al, *Carbon Nanotube Thin Films With Ordered Structures*,15 J. MAT. CHEM. 548 (2005); C.S. Du and N. Pan, *Supercapacitors Using Carbon Nanotubes Films By Electrophoretic Deposition*, 160 J. Power Sources 1487 (2006); C.S. Du and N. Pan, *High Power Density Supercapacitor Electrodes of Carbon Nanotube Films By Electrophoretic Deposition*, 17 NANOTECHNOLOGY 5314 (2006).

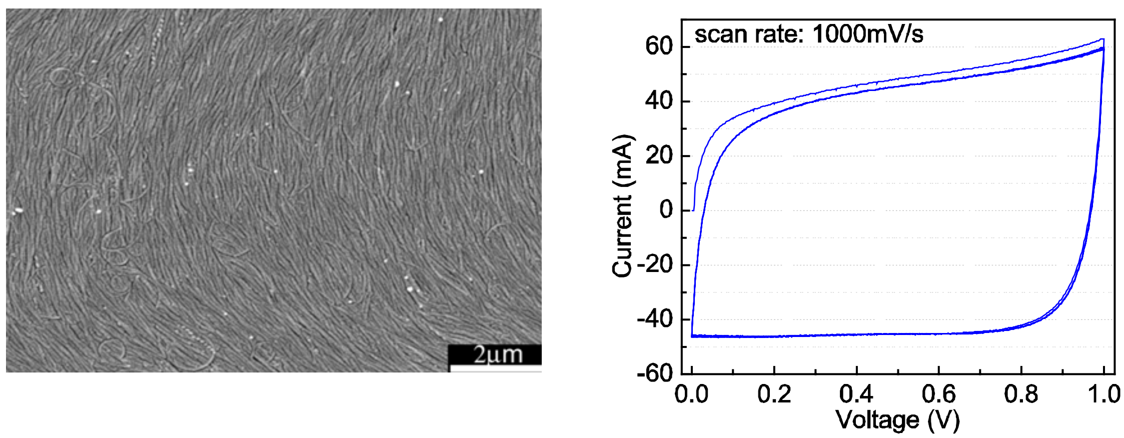
well. The cyclic voltammetry (CV) curve of supercapacitor electrodes thus fabricated exhibits close to an ideal rectangular shape even at exceedingly high scan rates of 1000mV/s (Figure 1(b)), an indication of a extremely small ESR. A specific power density of as high as about 30kW/kg was obtained. It is also important to note that properly functionalized carbon nanotubes are highly cohesive; therefore, the solid sheet electrodes can be made without using any binding materials.[28]

FIGURE 1

(a) SEM image of nanotubes thin film fabricated by depositing highly concentrated colloidal suspension, showing the local alignment of carbon nanotubes.

(b) CV curves at scan rates of 1000mv/s of an assembled supercapacitor using such nanotubes thin films as electrodes.

a.) b.)



Another approach is to fabricate carbon nanotube thin film electrodes using an electrophoretic deposition (EPD) method.[29] The supercapacitors built from such electrodes have exhibited an even better cyclic voltammogram at a high scan rate of 1000mV/s (Figure 2(a)), and a still high specific power density of about 20kW/kg was obtained. The reason that the power density of the capacitor by EPD is smaller than that of the capacitor by direct deposition is probably because the EPD electrodes were annealed in hydrogen and some nanotubes might have been etched. It worth noting that the supercapacitors showed superior frequency response, with a knee frequency about 7560 Hz (Figure 2(b)), more than 70 times higher than the highest knee frequency (100 Hz) so far reported for supercapacitors. The knee frequency denotes the maximum frequency at which capacitive behaviors is dominant, and is an indication of the supercapacitor response. An electrode with a higher knee frequency can be more rapidly charged and discharged.

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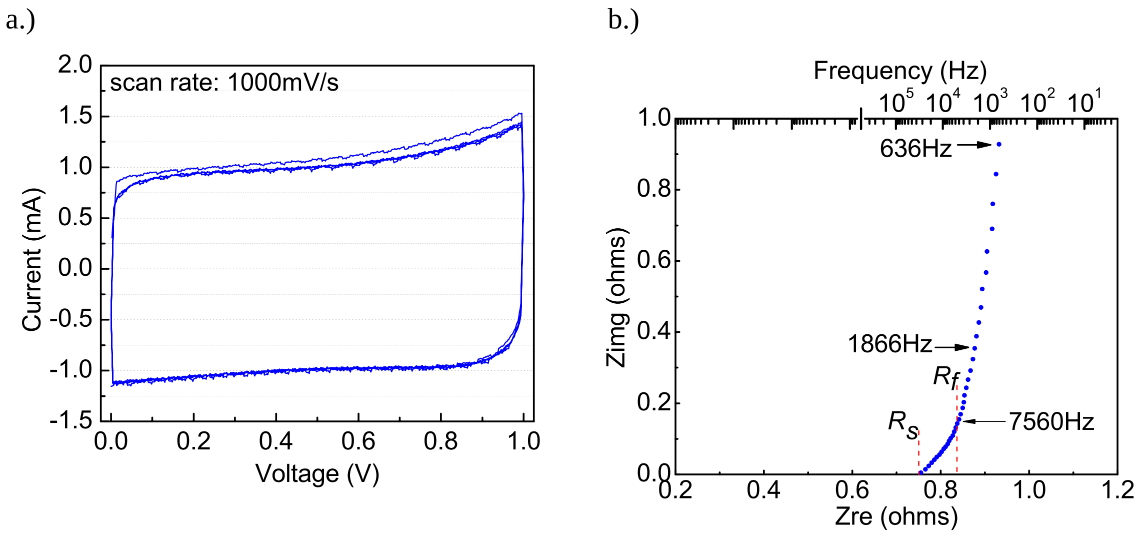
[28] Niu, *supra* note 18; C.S. Du, et al, *High Power Density Supercapacitors Using Locally Aligned Carbon Nanotube Electrodes*, *supra* note 27; C.S. Du, et al, *Carbon Nanotube Thin Films With Ordered Structures, supra* note 27.

[29] C.S. Du and N. Pan, Supercapacitors Using Carbon Nanotubes Films By Electrophoretic Deposition, supra note 27; C.S. Du and Pan, N., High Power Density Supercapacitor Electrodes of Carbon Nanotube Films By Electrophoretic Deposition,*supra* note 27.

FIGURE 2

(a) CV curves at a scan rate of 1000mV/s, and

(b) Complex-plane impedance of a supercapacitor made of EDP carbon nanotube thin film electrodes.



The EPD method has the advantages of short formation time, simple apparatus, and suitability for mass production. In addition, this technology allows for flexibility in the shape and size of the substrates on which the thin film is formed—essentially the resulting electrodes. All of these make EPD a highly attractive route in fabricating CNT electrodes for high performance supercapacitors and other similar devices.

It should be noted that, while high power density of the electrodes is critical for minimizing the size of power cell for miniaturized devices, the flexible nature of thin film electrodes is a benefit to some integrated power systems. Therefore, the high power density thin film electrodes have the potential to pave the way for a new generation of energy delivery system.

V. CONCLUSION

Carbon nanotubes are likely to have several advantages over conventional carbon materials for supercapacitor electrodes. In particular, nanotube-based supercapacitors are likely to demonstrate better power performance over conventional devices. Multi-walled carbon nanotubes are now being manufactured in large quantities at reasonable prices, which opens the possibility for cost-effective production of carbon nanotube-based supercapacitor electrodes. Yet, additional research and development is needed to bring nanotube-based supercapacitors to the market.

Market forces are driving the commercialization and adoption of high power density supercapacitors. Additionally, there is a need to minimize the power supply volume as well as to integrate flexible, thin-film supercapacitors into multilayer, laminate energy system such as batteries or fuel cells. Ultimately, if a scalable and cost effective technology for manufacturing high-performance nanomaterials-based supercapacitors is developed, we are likely to witness the large-scale adoption of these devices in a variety of areas.