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## ADVERTISEMENT



## Bifunctional carbon nanotube networks for supercapacitors

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Highly conducting and porous carbon nanotube (CNT) networks are used as the sole electron conducting material in supercapacitors. The high conductivity of CNT networks and the high surface area allow the replacement of both the metallic current collector and the active material that forms one side of the electrochemical double layer. The combination of both functions in one single layer leads to lightweight charge storage devices that can be manufactured using simple and cheap room temperature methods. The authors have demonstrated that the specific capacitance of such CNT electrodes is comparable to that of other carbon electrodes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2749187]

Charge storage devices, such as batteries, are nearing a point at which they cannot provide the peaks of power required without getting too big and too heavy.<sup>1</sup> A promising way to meet the future demands for high energy storage small size and lightweight—is to integrate advanced, so-called supercapacitors with batteries. Placed in parallel with the battery terminal, such a capacitor, in addition to significant storage capacity, provides a current boost on high load demands. This enhances the battery's performance, prolongs the run time, and extends the longevity of the battery.<sup>2</sup> Thus supercapacitors can allow batteries to meet current and future energy needs.

Carbon nanotube (CNT) networks have been recognized as attractive electrode material for supercapacitors. They offer the highest conductivity per weight and a high surface area. In comparison to amorphous carbon (a-C) electrodes, CNT networks have a higher conductivity since the high aspect ratio of the CNTs leads to a reduced number of contacts between the individual particles. Therefore, the same conductivity can be achieved with much less material. In addition, thick CNT networks form a freestanding film without any binder. Thick CNT networks are also mechanically more robust in terms of bending and abrasion. Taking these advantages into account, CNT electrodes seem well suited for use in electrochemical devices, and they have already been implemented in supercapacitors<sup>3-5</sup> and proposed for Li-ion batteries.<sup>6,7</sup> However, all previous publications in which CNTs have been used in a device adopted the architecture of commercial supercapacitors using metallic current collectors. In these cases, a-C is used as the electrode material with a high surface area but with a rather poor conductivity requiring a metallic foil on the back side as a highly conductive current collector.

In this letter, we evaluate the use of dense CNT networks as the sole electrically conducting material in supercapacitors. We propose a device architecture in which the high conductivity of thick CNT networks allows for the replacement of the metallic current collector, while at the same time, due to the high surface area, a network of this material can serve as the active material to build up the electrochemical double layer. The combination of both functions in one single layer leads to novel lightweight electrodes. Also, the use of one single material simplifies the device manufacturing.

A CNT (Ref. 8) suspension (0.1 mg CNTS/ml in 1% aqueous solution of sodium dodecyl sulfate as surfactant) was filtered through a filter membrane<sup>9</sup> (pore size: 20 nm) using a simple filter flask and moderate vacuum. The CNTs remain on the filter forming an entangled network. After washing and drying, the CNT network can be peeled off from the filter giving a freestanding CNT network and ready to use as electrode without any further treatment. The thickness of the film is roughly 20  $\mu$ m and the conductivity is about 10<sup>3</sup> S/cm. The capacitance was measured in a two electrode configuration. For that, the device is constructed in the following way: Two strips of a CNT network are fixed separately with double-sided scotch tape to a plastic substrate [polyethylenetherephthalate (PET)]. The overlapping



FIG. 1. (Color online) Sketch (left) and picture (right) of our supercapacitor using CNT networks for both the current collector and the electrode. The CNT network and the separator (white strip) are encapsulated in a PET container filled with electrolyte. Electrical contacts (on top) are made from silver paste.

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FIG. 2. Cyclovoltammogramm of a CNT network supercapacitor (solid line) and the ideal CV for a supercapacitor (dotted line).

parts of the substrate are glued together with a nitrocellulose membrane<sup>10</sup> (pore size of 2  $\mu$ m) as separator in between. The top part was left open to fill in the electrolyte (1*M* H<sub>2</sub>SO<sub>4</sub>). This way, the plastic is both support for the CNT network and encapsulant for the electrolyte. Cyclovoltammetry and galvanostatic charge/discharge experiments were used to determine the capacitance of the CNT electrode. For all measurements, a computer controlled potentiostat<sup>11</sup> has been used. In Fig. 1, a sketch of our CNT supercapacitor and a typical image of our device are presented.

A Cyclovoltammogramm (CV) of our device is presented in Fig. 2. The CV shows the typical CV of a dense CNT network. The peak at 0.35 V can be attributed to oxygen containing functional groups contributing as pseudocapacitance to the overall capacitance.<sup>12</sup> In general, functional groups, impurities, and an unoptimized conductivity lead to the difference to an ideal box-shape CV of a supercapacitor without internal resistance (dotted line).<sup>13</sup> From the CV, we calculated the specific capacitance c of our device according



FIG. 3. Galvanostatic charge/discharge curves at 1 mA of the CNT network.

TABLE I. Characteristics of the CNT network supercapacitor.

$R \\ (\Omega)$	$IR$ $(\Omega)$	C (F/g)	E (W h/kg)	P (W/kg)
25	137	39	0.02	5.8

to  $c=i/\nu$ , where  $\nu$  is the scan rate (20 mV/s) and *i* the corresponding current of the voltage applied. This way, we found the specific capacitance of our device to be 44 F/g at 1 V. This is in very good agreement to previously published results<sup>14–17</sup> even though these studies had used metallic current collectors or mixed CNTs with *a*-C. In Fig. 3, the result of a galvanostatic charge/discharge at 1 mA is presented.

Each branch of the entire curve starts with a voltage drop (IR drop) due to the internal resistance of our device. The relatively high value of about 137  $\Omega$  is mainly due to not optimized silver paste contacts. The slope of the discharge curve was used to determine the specific capacitance c of our device using  $c=i/\Delta E$ , where *i* is the current applied and  $\Delta E$ the voltage range. For the device shown, the specific capacitance was 33 F/g confirming qualitatively the results from the CV. It can be expected, that parameters such as the choice of CNT raw material, the treatment of the CNT material, and the right combination CNT material and electrolyte will minimize the internal resistance and maximize the device performance. All characteristics of our device in terms of the resistance of the CNT network (R), internal resistance of the device (IR), the capacitance (C), the energy density (E), and power density (P) are summarized in Table I.

Future work to optimize the proposed device architecture will address these issues. The authors would like to acknowledge Siegmar Roth (MPI, Germany) for technical support and Liangbing Hu (UCLA) for helpful discussions.

- <sup>1</sup>Nanotecture Ltd., www.nanotecture.co.uk, 2006.
- <sup>2</sup>Maxwell Technologies, Inc., www.maxwell.com, 2003.
- <sup>3</sup>C. Niu, E. K. Sichel, R. Hoch, D. Moy, and H. Tennent, Appl. Phys. Lett. **70**, 1480 (1997).
- <sup>4</sup>S. Shiraishi, H. Kurihara, K. Okabe, D. Hulicova, and A. Oya, Electrochem. Commun. 4, 593 (2002).
- <sup>5</sup>C. G. Liu, H. T. Fang, F. Li, M. Liu, and H. M. Chenga, J. Power Sources **160**, 758 (2006).
- <sup>6</sup>A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler, and R. E. Smalley, J. Electrochem. Soc. **147**, 2845 (2000).
- <sup>7</sup>S. H. Ng, J. Wang, Z. P. Guo, J. Chen, G. X. Wang, and H. K. Liu, Electrochim. Acta **51**, 23 (2005).
- <sup>8</sup>Produced by arc discharge method purchased as purified material (P3), CNI, Houston, TX.
- <sup>9</sup>Millipore Membrane Filters, Millipore Corporate, Billerica, MA.
- <sup>10</sup>Whatman Anodisc Membrane Filters, Whatman Inc., NJ.
- <sup>11</sup>Jaissle IMP 83-PC, Jaissle Electronic GmbH, Waiblingen, Germany.
- <sup>12</sup>Joseph N. Barisci, Gordon G. Wallace, and Ray H. Baughman, J. Electroanal. Chem. **488**, 92 (2000).
- <sup>13</sup>Elzbieta Frackowiak and Francois Beguin, Weld. Int. **39**, 937 (2001).
- <sup>14</sup>E. Frackowiak, K. Jurewicz, S. Delpeux, and F. Begiun, J. Power Sources 97-98, 822 (2001).
- <sup>15</sup>Soshi Shiraishi, Hideyuki Kurihara, Keiji Okabe, Denisa Hulicova, and Asao Oya, Electrochem. Commun. 4, 593 (2002).
- <sup>16</sup>Chen G. Liu, Hai T. Fang, Feng Li, Min Liu, and Hui M. Cheng, J. Power Sources 160, 758 (2006).
- <sup>17</sup>Chunsheng Du and Ning Pan, J. Power Sources 160, 1487 (2006).