Short communication

High-energy, rechargeable Li-ion battery based on carbon nanotube technology☆

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Abstract

In the near future, the portable power market will demand greater specific energy and power from lithium battery technology. These requirements cannot be met by conventional batteries or through extrapolation of the capabilities of conventional systems. New materials and systems must be developed to meet these stringent future requirements.

Nanomaterials offer a new exciting alternative to the standard materials traditionally used for fabrication of batteries. The work described herein, deals with a novel approach to the use of nanomaterials in the electrodes of lithium-ion batteries. We have synthesized and chemically modified carbon nanotubes and subsequently tested these modified nanotubes as electrodes in small lithium batteries. This paper describes electrochemical characterization of the novel electrodes as well as determination of the specific energy of simple one-cell batteries containing these novel electrodes. We have been able to demonstrate a laboratory cell with a specific exceeding 600 Wh/kg and pulse power exceeding 3 kW/kg.
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1. Introduction

Currently, carbon based materials from 0.1–10 μ are the choice for lithium storage in Li-ion batteries. Now, with the recent discovery of new crystalline forms of carbon, specifically single and multi-walled nanotubes with dimensions of 1–100 nm, it appears that there may be a new paradigm in carbon-based battery electrode materials. Nanotubes confer a high mobility to ion exchange processes, a fundamental for dynamic response of batteries based on lithium intercalation. For instance, recent experimental results have shown that it is possible to charge single wall carbon nanotubes up to one lithium for every three carbons and higher [1]. Lithium capacities of crude material have been determined experimentally to exceed 600 mAh/g [2,3]. In addition to the capacities of these materials, there are also some basic nan-

otube physiochemical properties that make them extremely attractive from a thin film polymer battery perspective. Although quite flexible, they have extremely high theoretical tensile strength (i.e. 50 GPa), with even greater shear strengths at nearly 500 MPa. Also, they have both a very high electrical conductivity at 10^4 Ωcm^{-1} and thermal conductivity at 2000–4000 Wm/K. In essence, this new generation of freestanding nanotube electrodes will offer durablility, flexibility, high electronic conductivity, the strength of steel and will simultaneously be able to deliver specific power and energy greater than any current lithium ion technology.

2. Experimental

2.1. Carbon nanotube synthesis

Single wall carbon nanotubes (SWNT) were prepared using the laser ablation process. Variables such as reactor temperature [4], laser power density [5], catalyst type [6], and raster program were adjusted accordingly in order to

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produce a broad range of SWNT materials. Specifics on the laser production of SWNTs has been described in the past [7], with the general experimental parameters summarized as follows: target: 4 g of 1–2 μ graphite-metal catalyst doped mixture pressed at 20,000 psi to a 30 mm × 5 mm disc. The graphite was doped with 0.3–1.2 at.% of each catalyst metal, Ni, and Co; atmosphere: 200–500 Torr, 100 sccm flowing argon atmosphere within 2.5 L quartz reaction vessel; laser: alexandrite 755 nm laser with a pulse duration of 100 microseconds and a 10 Hz repetition rate at 50–250 W/cm^2. Utilizing a GSI Lumonics mirror set, a linear sweep or step raster of a 2 cm × 2 cm grid pattern of the laser beam is programmed for a 0–50% overlap of each pulse striking the graphite target that is kept at 900–1200 °C with a Lindberg 3-zone furnace. Samples were refluxed in mineral acid for 6 h, filtered and washed with copious quantities of water.

Raman spectroscopy was used to monitor the variations of the SWNT materials before and after processing [8]. All spectra were obtained using a JY Horiba Raman Spectrometer with 632.8 nm laser excitation. The final product was a buckypaper as shown in Fig. 1.

2.2. Electrochemistry

Electrochemical testing began with of lithiation of specific 1 cm^2 pieces of various processed buckypapers using a 1 cm^2 lithium foil (Alfa Aesar) a nonwoven glass separator and 1 M lithium trifluoroethanesufonoimide (LiIm, 3M Co.) in 50:50 ethylmethyl carbonate (EMC):ethylene carbonate (EC). Lithiation proceeded for 20 h at 50 μA/cm^2. A two electrode electrochemical test cell was used for this purpose and the process was controlled using a Radiometer PGZ 301 electrochemical test apparatus. All testing was conducted in an Ar-filled glove box. Following lithiation, the cell was disassembled, cleaned and reassembled using the lithiated SWNT electrode as an anode and a pure SWNT electrode as the cathode. Fresh electrolyte (1M LiIm EC:EMC) and separators were employed. The cell was then cycled at various currents and the performance of the cell was recorded. Spe-

cific energies were calculated based on the average discharge voltage and the weight of the active electrode materials in the cell. A pulse power test was also conducted in which the cell was charged and then discharged for a brief period of time (<5 s) at high rate. The specific power of the cell was calculated from the average discharge voltage, the discharge current and the weight of the active electrode materials.

3. Results

Fig. 1 is a photograph of a 90 mm SWNT buckpaper prepared using the process previously described. This sample demonstrates the uniformity of the product and its mechanical resilience. Smaller pieces of this material were cut for testing.

Raman spectra of various carbon nanotube (CNT) materials are presented in Fig. 2.

The Raman spectra generated at 633 nm are due primarily to the metallic tubes that are resonantly enhanced by the incident laser. The intensity of the signals is directly related to the purity level of the sample. Qualitatively, thermal processing of the base washed sample appears to have dramatically increased the "purity" of the sample. This is evident from the intensity of the G-band BWF mode (at approximately 1600 cm^{-1}) that is directly related to the metallic SWNT content within the nanotube sample, i.e. proprietary thermal processing increases the purity of the SWNT sample.

Fig. 3 is a photograph of the simple two-electrode test cell used for the electrochemical evaluation of the CNT systems. This cell was also used to lithiate the SWNT anodes prior to cell assembly and subsequent cycle testing.

Fig. 4 is a brief cycle test of a typical test cell.

As shown here, the system appears to improve in performance with subsequent cycling. We believe this may be due the opening of the pores in the CNT electrode through penetration of the lithium and electrochemical oxidation of the nanotubes in the anode. These two cycles yielded an aver-
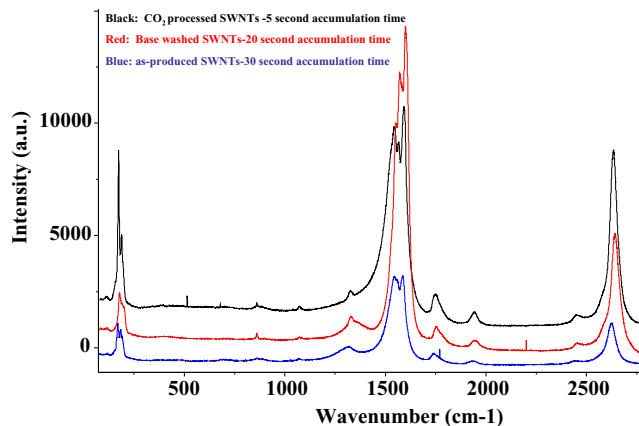

Fig. 1. Ninety millimeter diameter SWNT buckypaper.

Fig. 2. Raman spectra of SWNTs at different stages of thermal processing, 633 nm excitation.
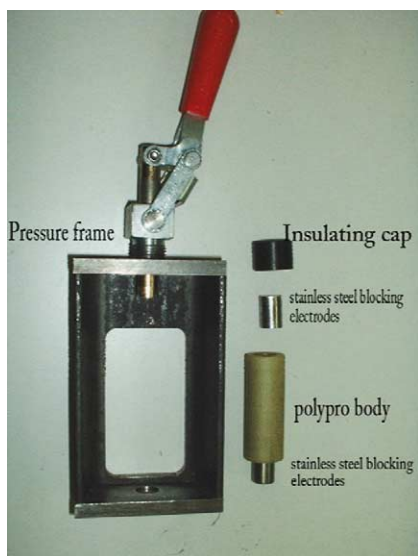
Fig. 3. Two electrode test cell 1 cm^2 active area.

Fig. 5. Successive cycles of thermally oxidized SWNT anode and pure SWNT cathode battery charged at 100 μA/cm^2 and discharged at 50 μA/cm^2.

age specific energy for this unpackaged laboratory cell of 263 Wh/kg. The second cycle alone, exhibited a specific energy of 285 Wh/kg.

Subsequent cycling of the cell resulted in better performance as the average voltage on discharge increased. Discharge cycle #4 yielded 411 Wh/kg, whereas discharge #8 resulted in 659 Wh/kg.

Fig. 5 shows the second set of cycles (red curves), the performance of the cell deteriorated, but still yielded an average specific energy of greater than 400 Wh/kg.

Although these results are based on the weight of the active material alone, one can envision that specific energies of greater than 200 Wh/kg are possible for these materials in a packaged system. In our estimation, the improved performance of the test cell with subsequent cycling may be caused by up to three separate factors: (1) the cell was discharged at a lower rate than it was charged thereby building charge in the anode (2) while the cell was held at >4 V the anode oxidized, which may have opened some of the SWNTs allowing for more effective re-lithiation with successive charges; and (3) the remaining nickel and cobalt catalyst metals within the processed SWNT buckypapers (from TGA data the amounts
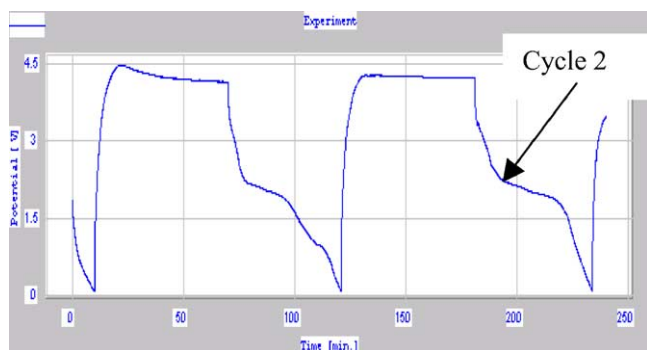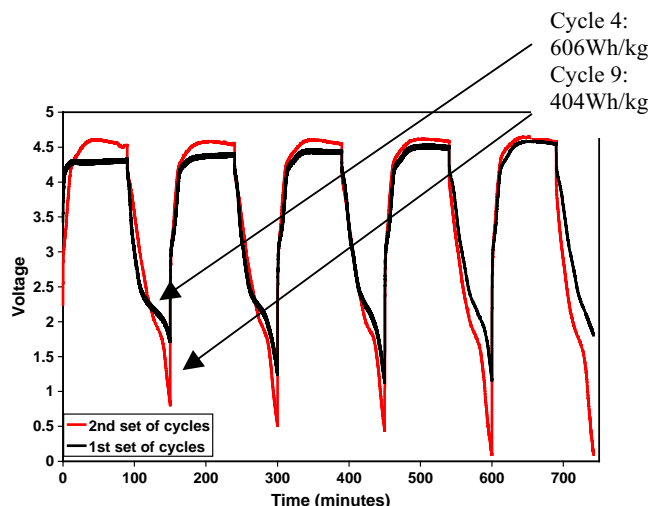
range from 4–8% w/w), from lithium nickel oxide and/or lithium cobalt oxide with cycling. Further analysis of these materials is ongoing. The improvement of performance with cycling phenomenon was witnessed many times (>20), during this research to varying degrees with different SWNT anodes (Fig. 5).

During the investigation the sample 1 cell was also evaluated to determine its pulse power characteristics. Fig. 6 shows that for this one pulse, the SWNT-cell maintained better than 1 V for 1.25 s at 1 mA discharge.

The active material in this cell weighed 0.3 mg, and the average voltage during discharge was 1.38 V, this yielded a peak pulse power output of 4.6 kW/kg. Although this result is based only on the mass of active materials, it demonstrates that it is possible to obtain both high specific pulse power and high specific energy from one SWNT-based system.

These preliminary results attest to the promise of using CNT materials in lithium batteries. Further work to perfect the processing of the CNTs to effect maximum capacity is underway. These efforts together with scaleup of produc-
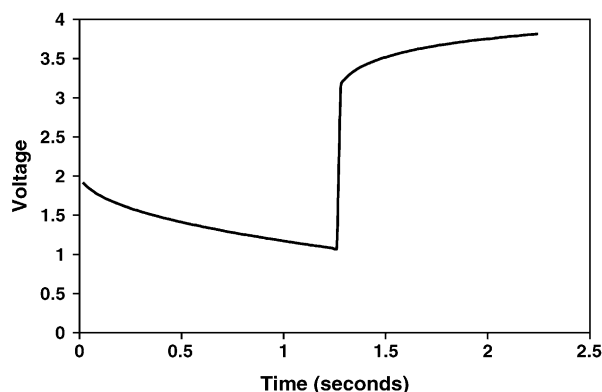

Fig. 4. NT2-30, 50 μAdscharge Ave. Specific energy 263 Wh/kg.

Fig. 6. Pulse power performance of the SWNT–SWNT rocking chair battery with 0.3 mg active material pulsed at 1 mA for 1.25 s.

tionshould eventually lead to cost competitive high energy CNT Li-ion batteries. In this regard, Companies such as Carbon Nanotechnologies, Inc. are scaling up mass production of SWNTs to kilogram quantities [9]. In addition, other firms including Nanoledge SA, are scaling up synthesis of nanotubes using the arc process to commercial quantities. A recent announcement [10] claims that Nanoledge and CNI project the cost of these materials to be around US$ 100/kg by the end of 2005. This is in-line with the current cost of mesocarbon microbeads, the conventional material of choice for Li-ion anodes.

Acknowledgements

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